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Automobile Sulfuric Acid Emission Control - The Development Status as of December 1975

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Automobile Sulfuric Acid Emission Control - The Development Status as of December 1975

a report to
the Administrator,
Environmental Protection Agency

prepared by
Emission Control Technology Division,
Office of Mobile Source Air Pollution Control,
Environmental Protection Agency

NATIONAL TECHNICAL
INFORMATION SERVICE
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March 17, 1976

ERRATA/ADDENDUM - 1

to

AUTOMOBILE SULFURIC ACID EMISSION CONTROL - THE DEVELOPMENT STATUS AS OF DECEMBER 1975

Corrections

The following corrections should be made to the above-captioned report:

Page 1-7 The third paragraph should be replaced with the following:

"Production lead time for the 1979 model year could become important for the improved air injection systems if development work is not started very soon. The advantages of improved air injection or improved fuel metering are not very apparent until standards of 0.41 HC and 3.4 CO along with sulfuric acid emission standards are required to be met. This is because air injection is considered more likely to be used to meet these more stringent HC and CO standards."

Appendix I, page I-17 An asterisk(*) should be added following the page heading "ADDRESSEES" and the following footnote should be added at the bottom of the page:

"A letter substantially the same as that reproduced on pages I-1 through I-16 was also sent to the Automobile Importers of America, requesting that that organization make available to its members copies of the information request and the outline."

Addendum

Control of air injection was indicated in the report to be a potentially promising technique to control sulfuric acid emissions. Little data were available on such systems at the time the report was prepared. Such a system has been tested recently. Preliminary, low mileage, tests on a Chevrolet Laguna with a controlled air injection system are shown below. The system is controlled by dumping the air injection.

The results may be confounded, because dynamometer bearings were replaced during the test sequence. The tests are to be re-run.

Table Addendum-1

	Gaseous Emissions, 1975 FTP(1) grams per mile			Sulfuric Acid Emissions, SC(2) (milligrams per mile)	
System Configuration	HC	CO	NOx	Average	Range
Full Air	0.51	3.56	1.57	32(3)	20 to 39.9
	0.45	4.65	1.53		
Average	0.48	4.10	1.55		
Controlled Air	0.33	3.61	1.56	9.6(4)	6 to 16.3
	0.36	5.28	1.39		
	0.31	5.21	1.38		
Average	0.33	4.70	1.44		

(1) LA-4 driving cycle, using the dilution tunnel, (2) Sulfuric Acid driving cycle and test procedure, (3) 8 tests, (4) 12 tests.

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AUTOMOBILE SULFURIC ACID EMISSION CONTROL -
THE DEVELOPMENT STATUS AS OF DECEMBER 1975

A Report to the Administrator,
Environmental Protection Agency

Prepared by

Emission Control Technology Division
Office of Mobile Source Air Pollution Control

December 1975

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EXECUTIVE SUMMARY

The sulfuric acid emissions from current production and prototype vehicles vary greatly as shown in Table 1-1.

Table 1-1
Sulfuric Acid Emissions from Baseline
Program Vehicles

Type of Emission Control System	Sulfuric Acid Emissions, mgpm* Range	Approximate Mean
Non-catalyst	0 to 3	1
Oxidation catalyst w/o air injection	0 to 118	8
Oxidation catalyst w/air injection	0 to 121	30
3-Way Catalyst	0 to 2	1

The most important parameter in the formation of sulfuric acid emissions appears to be the oxygen level in the exhaust gas to the catalyst. The significant difference in sulfuric acid emissions between the catalyst-equipped vehicles with and without air injection is attributed to this oxygen level effect.

Current technology which has demonstrated low (below 10 mgpm) sulfuric acid emissions has also demonstrated the capability to certify at the California emission levels of 0.9 HC, 9.0 CO, 2.0 NOx. About 20 percent of the estimated sales for 1976 in California have non-catalyst or catalyst without air injection control systems. Prototype 3-way catalyst vehicles, which also have low sulfuric acid emissions, have been successfully operated to 50,000 miles at emission levels below the California levels.

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*Milligrams per vehicle mile on the sulfuric acid test-procedure, the SC-7 with 300 ppm sulfur in the fuel. A milligram is one one-thousandth of a gram, or about 0.00004 ounces.

The most promising future sulfuric acid control technique is control of the exhaust gas oxygen levels by improved fuel metering systems and/or improved air injection systems. Oxidation catalyst, 3-way catalyst, and dual catalyst emission control systems are all compatible with oxygen level control systems. Other important control techniques may be developed as sulfuric acid control system development programs are commenced. Most of the experimental work which has been done to date has been related to the characterization of production emission control systems, and relatively few data are available on advanced systems, especially those designed with sulfuric acid control in mind.

However, meeting standards more stringent than 0.9 HC, 9.0 CO, 2.0 NOx gaseous emissions while controlling sulfuric acid emissions is not precluded. The degree of difficulty in meeting more stringent HC and CO emissions may be increased, depending on the control techniques used.

Production lead time for the 1979 model year could become important for the improved air injection systems if development work is not started very soon. The advantages of improved air injection or improved fuel metering are not very apparent until the 0.41 HC and 3.4 CO levels.

The lack of a finalized test procedure for sulfuric acid emissions and the lack of a sulfuric acid emission standard have caused some manufacturers to defer from starting serious development programs. The test procedure is still being developed by EPA. The Notice of Proposed Rule Making, (NPRM) is now scheduled for publication in May of 1975. Variability in test results over the sulfuric acid test cycle, the SET, has continued to be a problem, for EPA and the manufacturers. This problem is expected to be alleviated as more is learned about sulfuric acid emissions and the test procedure is standardized.

From the manufacturers' point of view, the HC, CO, and NOx emission standards need to be firmed up for the 1979 model year. Not doing so within the next few months could result in lead time problems if stringent HC, CO and NOx levels are instituted, in conjunction with stringent sulfuric acid standards.

SECTION 2

INTRODUCTION AND BACKGROUND

2.1 Introduction

This report has been prepared to summarize the current status of sulfuric acid emission control technology development and to provide information for the Administrator and others within EPA on the impacts of approaches likely to be used to control sulfuric acid emissions.

The information used to prepare this report came from four main sources: 1) EPA in-house testing, 2) contracted efforts sponsored by EPA, 3) the technical literature, and 4) information supplied to EPA by automobile manufacturers and others at the request of EPA. A copy of the letter requesting the information, a list of the information desired, and a list of the organizations to which the request was made can be found in Appendix I of this report.

This report does not contain any discussion of or conclusions about the health effects of sulfuric acid or the air quality impact of sulfuric acid emissions.

2.2 Background

Interest in sulfuric acid emissions from automobiles became greatly expanded during 1973. In 1972 tests for particulate emissions run by an EPA contractor showed that the particulate emissions from vehicles equipped with oxidation catalysts and run using unleaded fuel were higher than the particulate emissions from non catalyst-equipped vehicles, also run using unleaded fuel. This was not generally expected at that time since the majority of the particulate from non catalyst-equipped vehicles, run using leaded fuel was found to be lead, and the use of unleaded fuel was expected to reduce the particulate emissions from both catalyst-equipped vehicles and non catalyst-equipped vehicles to the same extent.

Since the catalysts in question had been furnished by the Ford Motor Company, they requested and were given the filters used in the particulate testing; subsequent analysis showed the presence of sulfuric acid. Ford informed EPA of the results of their analysis in a February 5, 1973 letter from Mr. H. L. Misch to Mr. Robert Sansom, then the Assistant Administrator for Air and Water Programs of EPA.

EPA began to expand its work to characterize sulfuric acid emissions from motor vehicles soon after that.

On March 8, 1974 a notice was published in the Federal Register requesting the submission of information about measurement methods and control technology for sulfuric acid emissions.

The sulfuric acid issue was also discussed at two public hearings held by EPA early in 1975. These two public hearings were the hearings on the applications for suspension of the then 1977 HC and CO standards, and a related hearing on sulfuric acid emissions.

The Decision of the Administrator of EPA on the applications for suspension of the 1977 HC and CO standards discussed the sulfuric acid issue extensively. In that Decision, the Administrator indicated that EPA would soon publish a Notice of Proposed Rule Making (NPRM) for a sulfuric acid emission standard. The standard was targeted to be applicable to motor vehicles for the 1979 model year. Since that time, EPA has embarked on an intensive program to determine the impacts of various motor vehicle standards, to develop certification feasible test procedures, and to publish the NPRM. At the time of this report, the target date for publication of the NPRM was May 1976.

2.1 Nomenclature

The gaseous emissions results in this report are reported in the usual triplet abbreviation in the following manner: 0.41 HC, 3.4 CO, 1.2 NOx, which means 0.41 grams per mile hydrocarbons, 3.4 grams per mile CO, and 1.2 grams per mile NOx, all gaseous emissions determined on the 1975 Federal Test Procedure (FTP). Since this report deals with sulfuric acid emissions, the report team has added another abbreviation to the triplet to correspond to milligrams per mile (mgpm) of sulfuric acid (H_2SO_4). The test procedure for sulfuric acid is just in the process of being finalized, and the report team has used values for sulfuric acid emissions based on the latest test cycle, the so-called sulfate cycle number seven (SC7). The test procedures are discussed in Appendix II. A vehicle that achieved the abovementioned gaseous emissions on the 1975 FTP and for example 20 milligrams per mile sulfuric acid on SC7 would be reported as 0.41 HC, 3.4 CO, 1.2 NOx; 20 H_2SO_4.

Other notations that may be used are LA4 which is the Federal urban driving cycle used for the FTP; the 1972 FTP which is the older, no longer used, version of the 1975 FTP which does not include the hot start; SC1 and other numbers which are earlier versions of the sulfuric acid cycle. Other test conditions for which there are data are at steady state cruise. These are labeled "SS". For example 60SS means 60 miles per hour, steady state cruise.

Other abbreviations that may appear are FET (for fuel economy test) and HWFET (for highway fuel economy test). These both refer to the EPA Non-Metropolitan Driving Cycle. This cycle is used by EPA to determine what are referred to as highway fuel economy numbers.

Fuel economy is reported in miles per gallon (MPG). MPG Values determined on the 1975 FTP are labeled MPGU ("U" for urban) and values determined on the Non-Metropolitan Driving Cycle are labeled MPGH ("H" for highway). Results labeled MPGC are a composite value from the following relationship:

MPGC = 1/((.55/MPGU) + (.45/MPGH)).

The abbreviation used for inertia weight is IW. Inertia weight refers to the test weight used for gaseous emissions, sulfuric acid and fuel economy determinations.

All sulfuric acid emission results from gasoline fueled vehicles have been converted to the equivalent basis of a fuel containing 0.030 percent by weight sulfur. This is a sulfur level considered to be the most typical of the average unleaded, regular fuel currently available. The conversion was done by linear ratio of the sulfur levels of the fuel. As an example, a vehicle that got 12 H_2SO_4 on 0.010 percent by weight sulfur fuel would be converted to 12 (0.030/0.010) = 36 H_2SO_4.

For distillate-type fueled vehicles, such as Diesels, the same procedure was followed except in this case the value of the average fuel was taken to be 0.21 percent sulfur by weight.

SECTION 3

CONCLUSIONS

Caveat

In a field such as emission control technology in which rapid developments and increases in understanding are continually being made, any conclusion must be viewed with the understanding of the time at which it was made. This is and has been the case for gaseous emission control technology and is even more true for sulfuric acid emission control technology.

Conclusions

- Control of sulfuric acid emissions from automobiles is still in the infant stage of development.

Manufacturers are working now in 1975 to meet an unknown standard for model year 1979. This can be compared to the years 1970-1971 when they were working to meet known standards in 1975-1976. This report concludes that the situations are similar - new test procedures -new technology needed - and a position very low on the learning curve. Many techniques and approaches for controlling sulfuric acid emissions remain to be explored.

- Domestic manufacturers are somewhat ahead of most foreign manufacturers in preparing to meet sulfuric acid standards.

The clear message from the responses to EPA's request for information on the studies of sulfuric acid emissions from the majority of the foreign manufacturers was that they are waiting to see what final test procedures and standards will be proposed before they mount an effort to meet the standards. Some of the foreign manufacturers do not even have the test equipment needed to measure sulfuric acid emissions, let alone have data and rational development plans. Though in fairness, some foreign manufacturers, particularly Toyota and Nissan, have made significant contributions to the understanding of sulfuric acid emissions despite the long lines of communication between EPA and their research centers.

- Some manufacturers appear to be concerned about the variability of test results, and will probably maintain that EPA has no business setting standards until the test results are less variable.

It is true that the test procedures for sulfuric acid testing are relatively new and that some important parts of the certification-feasible procedures currently remain to be finalized (especially the vehicle preconditioning). However, test result variability for both gaseous emissions and sulfuric acid emissions has always been a combination of both test procedure variability (driver, sampling, analyses, etc.) and vehicle variability (the vehicledoes not perform exactly the same way on each test). The manufacturers always strive to reduce vehicle variability, and based on their comments and EPA's own work, EPA strives to reduce test variability. This has always been the case with gaseous emissions and will likely continue to be the case with sulfuric acid emissions, although it is true that the causes of vehicle variability during sulfate testing are relatively unexplored now.

- Considering the abovementioned caveat and the preceding conclusions, the analyses conducted in concert with this study resulted in estimates of the sulfuric acid emission levels that could be met in 1979 for various concurrent gaseous emissions standards as shown below.

Table 3-1
Ranges of Sulfuric Acid Emission Levels and Gaseous Emission Standards for Model Year 1979

Gaseous Emissions (grams per mile, 1975 FTP)			Sulfuric Acid Emissions (milligrams per mile, SET)
HC	CO	NOx	H2SO4
1.5	15	3.1	5-15
1.5	15	2.0	5-15
0.9	9.0	2.0	5-15
0.9	9.0	1.5	5-15
0.41	3.4	2.0	5*-50
0.41	9.0	1.5	5*-50
0.41	3.4	1.0	5*-50
0.41	3.4	0.4	5*-50

At this point in time, the best estimates that can be given involve the use of ranges. There are four basic reasons for this:

1. The technology for controlling sulfuric acid emissions is just now being considered for development.

2. There is variability in the test results now and the test procedure is still not finalized.

3. Several different technical approaches could be used to meet the gaseous emission standards and their likely sulfuric acid emissions are not the same.

4. Not many sulfuric acid emission data are available from advanced gaseous emission control systems that were designed without consideration for sulfuric acid emissions, let alone systems that were designed with sulfuric acid emission control in mind.

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* The lead time for the introduction of 3-way catalysts by all manufacturers and the 50,000 mile durability of 3-way catalysts at these gaseous emission levels is uncertain.

As time goes by and the technology and understanding advances, the ranges will, of course, narrow.

The deterioration factor assumed for the sulfuric acid emission levels is 1.0 to reflect maximum sulfuric acid emissions at the 4,000 mile point. The lower bound of the sulfuric acid emissions in table 1-1 represents the lowest technically achievable standard for sulfuric acid at the given gaseous emission standard. Thus this maximum effort for sulfuric acid control is assumed to force 3-way catalyst technology at the .41 HC levels and no catalyst or low excess air, catalyst technology at the .9 HC levels. This estimate would involve the greatest effort on the part of the manufacturers. This also means that it will be more difficult to certify at both the given gaseous and sulfuric acid levels. The highest level in the range assumes only moderate technological improvements and leaves more technological options open to the manufacturer. This highest level also involves a much lower risk of all manufacturers being able to certify. These ranges include lead time, variability, and technological considerations; however it does not mean that all currently produced emission control systems of each manufacturer will be capable of certification.

Table 1-1 should not be interpreted to mean that low gaseous emission levels cannot be achieved along with low sulfuric acid emissions. Three-way catalysts have the potential to do both. Also, other technologies, particularly limited AIR oxidation catalyst approaches are still relatively unexplored. What should be interpreted from table 1-1 is that it would be more difficult for the manufacturers to certify vehicles at both stringent sulfuric acid and gaseous emission standards.

It should be recognized that, as with emission control systems for regulated gaseous emissions, EPA does not dictate the control technology to be used to control sulfuric acid emissions. That choice is left to the individual vehicle manufacturers. EPA only establishes the level that the manufacturers' vehicles are required to meet for each pollutant.

As the gaseous emission standards and the sulfuric acid emission standards become more stringent, however, the number of system choices open to the manufacturers becomes more limited.

- Manufacturers that are doing anything at all in sulfuric acid emission work, currently appear to be doing more in the procedures area than in the systems development area.

There could be several reasons for this. The manufacturers could be waiting until they are forced to meet a sulfuric acid emission standard, via promulgation of one. However, there are other factors that must be considered. Developing an expertise in the test procedure area is one important first step, and it is arguable whether series or parallel control technology development is a more optimal approach. Additionally, the capabilities of the manufacturers may be strained so that development of everything needed is slower than desirable. Consider the emissions for 1974 - HC, CO and NOx were the only requirements. For 1979 the manufacturers will be facing still uncertain gaseous emissions standards, high altitude regulations, a new evaporative procedure and standard, and a new light duty truck standard. Coupled with this is the pressure to produce vehicles with better fuel economy. Yet another factor is that EPA has asked the manufacturers for assistance in obtaining procedures information.

The report team considers that all of the reasons discussed above have contributed to the current status.

- The general technical approaches now under study for controlling sulfuric acid emissions appear to be improved fuel management, control of oxygen level in the exhaust, and catalyst modifications.

The approaches listed above are similar to some of those also being pursued for control of gaseous emissions control at more stringent gaseous emission standards.

SECTION 4

WHAT CAUSES SULFURIC ACID EMISSIONS?

4.1 Parameters Governing Sulfuric Acid Formation

Almost all fuel used for motor vehicles contains sulfur to one degree or another. The current national average sulfur level for gasoline is approximately 0.03% and for Diesel fuel No. 2 is 0.21%. This sulfur is usually in the form of organic sulfur compounds. These sulfur compounds, during the combustion process, are oxidized to sulfur dioxide (SO_2) and sulfur trioxide (SO_3). By far the greater quantity of sulfur oxides from the combustion is SO_2, with only a very small amount of SO_3 formed. Sulfur trioxide combines readily with water (H_2O) to form sulfuric acid (H_2SO_4). In the exhaust of motor vehicles there is abundant H_2O, since H_2O is one of the major products of combustion (CO_2 being the other), and there is about one kilogram of water formed for each kilogram of fuel burned. The sulfuric acid thus formed in the exhaust system and a short distance beyond the vehicle tailpipe is emitted to the atmosphere in droplets small enough to be called a mist.

The major factors that govern the production of sulfuric acid are; a) the sulfur content of the fuel, b) the conditions during combustion and in the exhaust system including temperature and oxygen concentration, c) the time history of the exhaust, e.g. residence time, and d) the amount of water present. Since the assumption is usually made that there is enough water present, the important consideration is the oxidation of SO_2 to SO_3. An example of the influence of temperature and oxygen level in SO_2 to SO_3 oxidation is shown in Figure 4-1* and in Table 4-1*. One can see from Figure 4-1 that lower temperatures and

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*Letter to Dr. Joseph Somers, EPA, from Dr. K. Bachman, Exxon Research and Engineering, July 17, 1975.

Figure A-1

Equilibrium Conversion

$SO_2(g)+1/2\ O_2(g) = SO_3(g)$

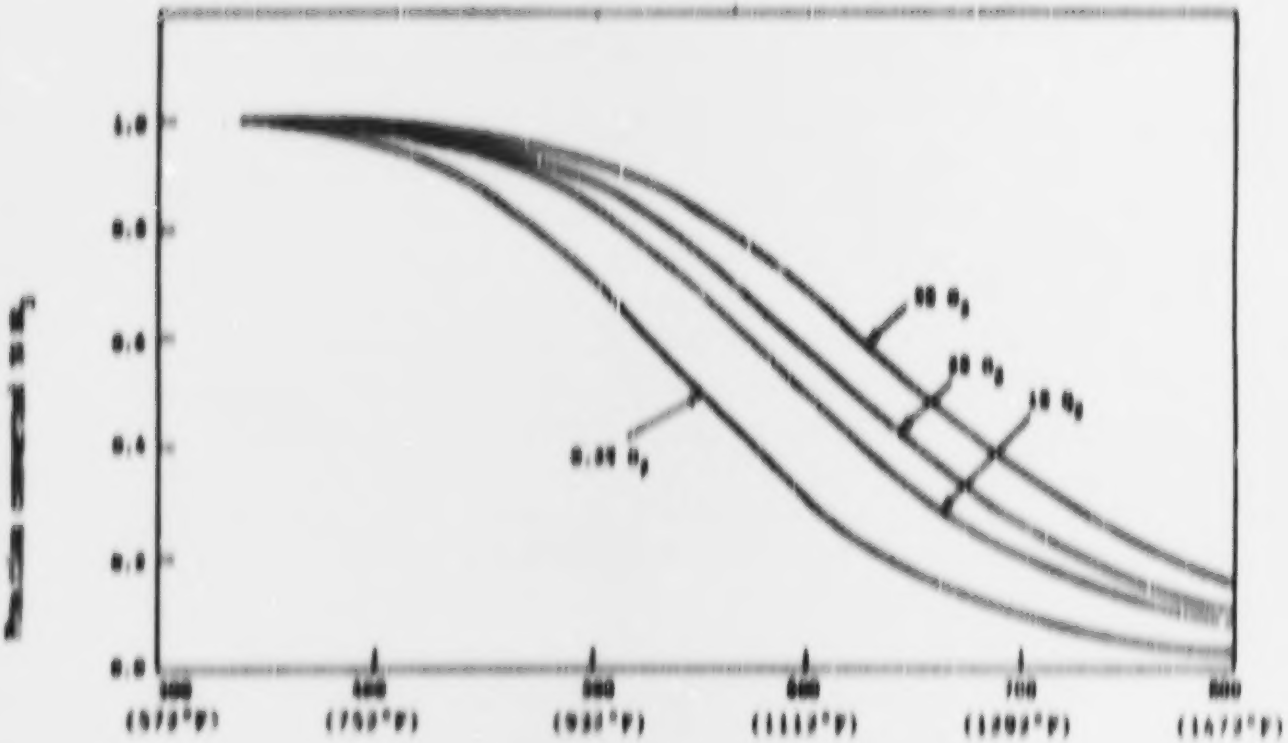


Table A-1

Equilibrium Conversion of SO_2 to SO_3

Percent O_2		% Conversion SO_2 to SO_3			
		[illegible]	[illegible]	[illegible]	[illegible]
Temperature					
°C	°F				
[illegible]	752	[illegible]	[illegible]	[illegible]	100
[illegible]	842	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	932	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	1022	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	1112	[illegible]	[illegible]	[illegible]	[illegible]

higher oxygen levels enhance the equilibrium conversion of SO_2 to SO_3. Of course, these values represent equilibrium or theoretical maximum conversion,and kinetics governing reaction rates determine actual conversion values as discussed below.

4.2 Sulfuric Acid Production Over Catalysts

Figure 4-1 shows the equilibrium conversion of SO_2 to SO_3 and is indicative of what would be produced if the reactants were held at the given temperature and oxygen concentration for a long time. Since all chemical reactions take a finite time to reach equilibrium, the amount of SO_3 formed may be less than is indicated by Figure 4-1 if the time available is too short. What is not shown on Figure 4-1 is the _rate_ of reaction to form SO_3 from SO_2. The reaction rate is what determines how long it takes for the reaction to go to the equilibrium conditions.

The production of sulfuric acid over catalysts is important, because what a catalyst does is speed up the reaction rate. In fact, most of the sulfuric acid produced for industrial use is produced by a catalytic process. In the context of industrial use, sulfuric acid is a valuable and important chemical that has many uses because it is a strong acid with a high boiling point, a good oxidizing agent, a good drying and dehydrating agent, and is also relatively cheap.

The contact process for sulfuric acid production involves the production of SO_2, passage of SO_2 and oxygen over a catalyst bed to form SO_3, and the formation of sulfuric acid by passing the SO_3 through concentrated sulfuric acid to which water is continually added. The basics of the contact process were first reported about 1831.

Both platinum (Pt) catalysts and vanadium pentoxide (V_2O_5) catalysts can be used for the contact process, with V_2O_5 having greater resistance to arsenic poisoning.

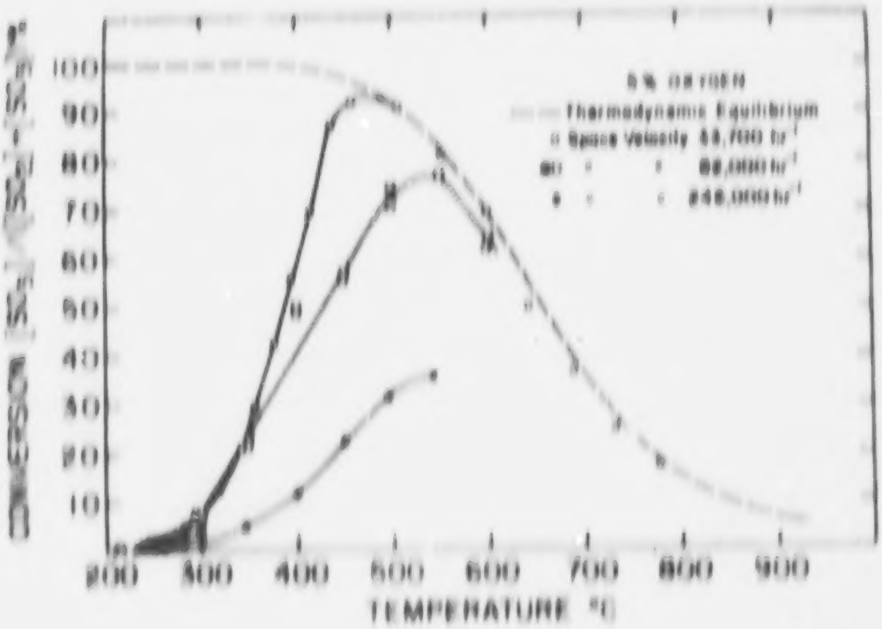
Since automotive catalysts use platinum as one active material it can be expected that some sulfuric acid production potential is there, since there are oxygen, SO_2, water, and a platinum catalyst present.

There are many parameters governing sulfuric acid production over automotive catalysts. Among them are catalyst temperature, space velocity, noble metal composition and dispersion, washcoat composition, surface area, and preparation, catalyst processing and pre-treating, type of substrate and storage characteristics, exhaust gas oxygen level, effect of other exhaust gas constituents, and sulfur dioxide concentration. The effects of these parameters are discussed below:

Catalyst Temperature

Theoretically, catalyst operating temperature is expected to have a significant effect on sulfuric acid formation. The thermodynamic equilibrium constant for SO_2 oxidation is such that higher temperatures lead to decreased sulfuric acid formation. Also, the temperature and activation energy required determine the kinetics for the reactor, i.e., the rate at which the reaction occurs. Lab data using automotive catalysts show that at high temperatures the lab results approach equilibrium predictions and at low temperatures the lab results are far from the equilibrium predictions. This indicates that the reaction rates at high temperature are high enough to permit equilibrium to be approached, and that the reaction rates at low temperatures are sufficiently low to make equilibrium predictions of little value. Unfortunately, automotive catalysts operate most of the time in the intermediate temperature range where SO_2 oxidizes readily. Low temperature operation is not feasible because HC and CO oxidation would also be very slow. High temperature operation of the catalyst can result in poor physical and/or chemical durability. Figure 4-2* shows the relationship between conversion rate and temperature for certain space velocities (reciprocal of residence time).

Table 4-2
Effect Temperature and Space Velocity
on SO_2 Oxidation



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*Ford Motor Company Report on Light Duty Vehicle Sulfuric Acid Emission Control Status, September 2, 1975.

The theoretical benefits of higher temperature may be attainable with satisfactory durability if improved active material temperature stability and substrate integrity are achieved. Conventional catalysts are continually being improved in these respects. Perovskite catalysts, which hold the active materials in a crystal lattice, are a relatively new approach which appear to offer some promise in this area.

Space Velocity

Space velocity, in effect, determines the total time period in which the exhaust gas is in contact with the catalyst. Space velocity is the exhaust flow (ft^3/hr) measured at standard temperature and pressure, divided by the catalyst volume (ft^3). The reciprocal of space velocity is contact time, usually expressed in hours, that the exhaust gas is exposed to the catalyst. Lab data show that sulfuric acid emissions are affected by space velocity, with a low space velocity tending to increase sulfate emissions. This was shown in Figure 4-2. GM reported the data shown in Table 4-2 which also shows increased sulfuric acid conversion at lower space velocities.

Table 4-2
Effect of Space Velocity on Sulfuric Acid
Formation in Pelleted Catalysts

Space Velocity	Sulfuric Acid Formation
7,000 hr^{-1}	18%
28,000 hr^{-1}	14%

The effect of space velocity on sulfuric acid formation must be taken into consideration in the optimization of catalyst type and size.

Noble Metal Composition

Noble metal composition appears to have an effect upon sulfuric acid conversion. Alternative noble metals for oxidation catalysts include platinum (Pt), paladium (Pd), and rhodium (Rh). Table 4-3 shows a comparison of Pt, Pt-Pd and Pt-Rh catalysts. The test vehicle was a Plymouth Fury with a 318 cu. in. engine and AIR. The catalysts were Chrysler-UOP monoliths.

Table 4-3
Comparison of Sulfuric Acid Emissions for
Different Noble Metal Catalysts

Catalyst Composition	Speed(mph)	Sulfuric Acid Emissions(mgpm)
platinum (fresh)	30	71
	60	98
platinum/paladium	30	31
(fresh)	60	80
platinum	30	17
(500 miles aged)	60	80
platinum/paladium	30	25
(500 miles aged)	60	81
platinum/rhodium	30	18
(50 miles aged)	60	55

Tailoring the noble metal composition to reduce sulfuric acid emissions while maintaining HC and CO conversion efficiency is considered feasible, although rhodium is not considered to be an immediate solution to the sulfuric acid problem as much now as it was initially because of the poorer durability of current Pt/Rh catalysts.

Catalyst Dispersion and Washcoat

Very limited data is available at this time on the effects of noble metal dispersion and washcoat on sulfate formation. The washcoat especially can affect the storage and release process, due to its large surface area and mass, compared to the active material. Chrysler has also reported some promising test results using DuPont developed perovskite catalysts. These catalysts have the noble metal dispersed in a perovskite crystal structure. Chrysler did not report actual test data, but did claim that a 30% decrease in sulfuric acid formation was experienced using perovskite catalysts. This type of catalyst is also claimed to be resistant to lead poisoning.

Catalyst Processing and Pre-Treating

This appears to be a promising area for sulfuric acid control. It is known that techniques such as aging decrease a catalyst's sulfuric acid formation capabilities. Table 4-4 shows data reported by Chrysler on the effect of artificial aging.

Selective catalyst poisoning may also hold promise. For example it is known that arsenic and lead will poison the SO_2 to SO_3 formation over a platinum catalyst. It may be possible to poison this reaction while not significantly reducing the HC and CO oxidation capabilities of a catalyst. However, an important unknown factor at this time is the effect on catalyst durability of aging and/or selective poisoning. It seems clear that this approach to sulfuric acid control merits a great deal of attention.

Table 4-4
Effect of Artificial Aging of Catalysts
on Sulfuric Acid Emissions
(Synthetic Exhaust, 1000°F, 22,000 ghsv)

Catalyst*	Preconditioning	% Conversion, SO_2 to H_2SO_4
Pt monolith	None	40%
Pt monolith	88 hours at 1600°F in air	20%
Pt monolith	16 hours at 1800°F in air	20%
Pt monolith	After addition of .25% lead from lead nitrate solution	20%

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*Each of the four catalysts tested were unaged prior to preconditioning for the test.

Type of Substrate and Storage Characteristics

Two major types of substrate exist, monolithic and pelleted. It is not clear at this time whether monoliths andpellets have significantly different SO_2 conversion characteristics. In theory, differences may exist because the two types have dissimilar physical, chemical, and thermal properties. The sulfuric acid storage characteristics of the two are also dissimilar and this has clouded experimental efforts to evaluate their conversion characteristics.

The differences in storage behavior are thought to be due to the different mass amounts of alumina in monolithic and pelleted catalysts. Storage of sulfur compounds on catalysts is believed to be caused by a chemical bonding between these compounds and the alumina. Pelleted catalysts are composed of semi-porous alumina pellets whereas monolithic catalysts have a cordierite substrate with only a thin washcoat of alumina. The greater mass and surface area of alumina and the slower warmup (sulfur compounds store more readily on colder surfaces) present in pelleted catalysts both contribute to increased sulfuric acid storage. Pellets have a slower warmup because they have greater thermal inertia than the thin walled monolithic substrate.

Figures 4-3[4] through 4-6[4] show the effects of preconditioning on sulfuric acid emissions. Both the pelleted and monolithic catalysts were preconditioned on each fuel by a sequence of standard AMA durability mileage accumulation followed by a series of cold start and hot start 1975 FTPs. The varying sulfuric acid emissions as a function of time show the adsorption and desorption that takes place until stability is reached.

Oxygen Level

Catalytic emission control systems generally operate with a significant amount of excess oxygen in the exhaust in order to insure conversion of HC and CO. The amount of excess oxygen appears to be an important parameter in determining the level of SO_2 to SO_3 conversion. Figures 4-7[4] and 4-8[4] show laboratory reactor data for monolith and pelleted catalysts.

It can be seen that SO_2 conversion drops off considerably as the excess O_2 level is lowered to 0.5% and below. It is noteworthy that the CO conversion rate remains high at 0.5% excess oxygen. The investigators who reported this data indicated that the HC conversion behavior paralleled the CO behavior.

The selective oxidation of HC and CO demonstrated at low excess oxygen levels indicates that close control of excess oxygen via improved

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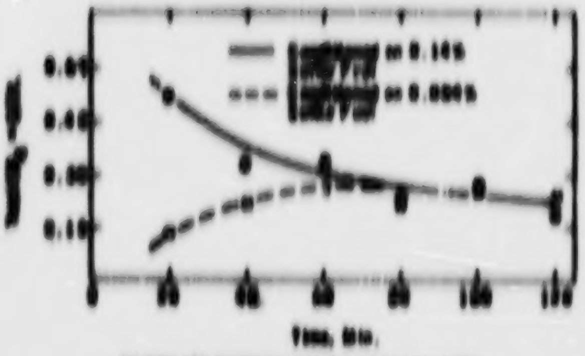
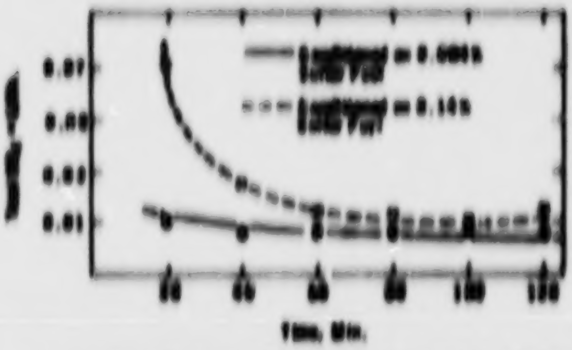
[4] M. Beltzer, R. J. Campion, J. Harlan and A. M. Hochhauser, The Conversion of SO_2 Over Automotive Oxidation Catalysts, SAE Paper 750095, February 1975.

Figure 4-3



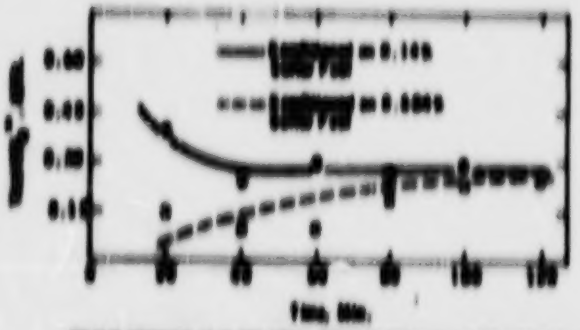
[illegible]

Figure 4-4



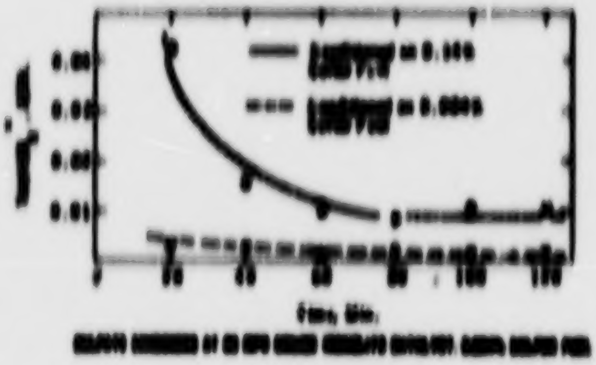
[illegible]

Figure 4-5



[illegible]

Figure 4-6



[illegible]

fuel metering or modulated air injection is a promising control approach for sulfuric acid. The low sulfuric acid emissions exhibited by three-way catalyst systems, which have precise control of the exhaust oxygen level, support the theory that selective oxidation of HC and CO can be accomplished.

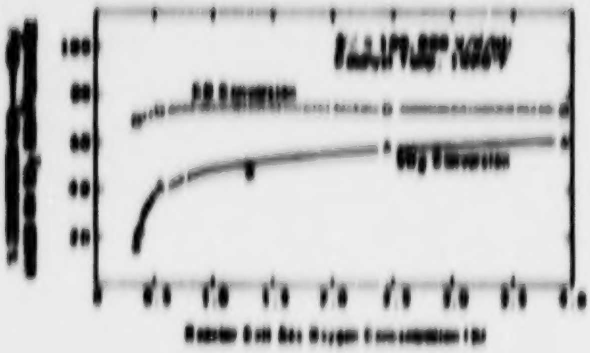
Effect of Other Exhaust Gas Constituents

It has been shown that the presence of exhaust gases such as carbon monoxide, propylene (C_3H_6) and hydrogen tend to reduce the conversion of SO_2. Figure 4-9 contains data reported by Ford which shows the effect of these gases.

The probable explanation for this behavior is that the reducing gases compete with the SO_2 for adsorption on the catalyst and the available oxygen. Carbon monoxide and propylene are preferentially oxidized under these circumstances rather than SO_2. This phenomenon could be utilized as a control technique but precise air-fuel ratio or air injection rate control would be needed in order to maintain the catalyst at near breakthrough condition. Breakthrough occurs when conditions are such that significant HC and CO pass entirely through the catalyst without reacting because of insufficient residence time.

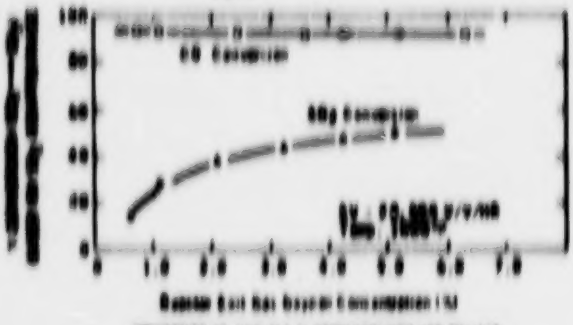
Another exhaust gas constituent which could possibly affect sulfuric acid formation is lead. The conversion of lead to lead sulfate in the exhaust has not yet been investigated. The disadvantages of the use of more lead in the fuel may be why this effect has not been studied. These disadvantages include increased deposits on spark plugs and EGR valves and catalyst deactivation. In addition to lead, lead sulfate may also have detrimental health effects.

Figure 4-7



CONVERSION VS EXIT GAS OXYGEN CONCENTRATION FOR MONOLITH

Figure 4-8



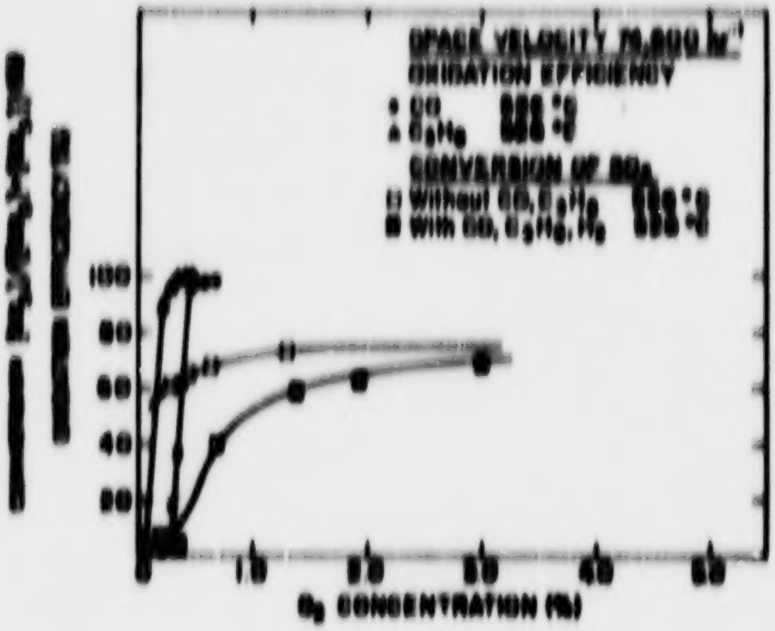
CONVERSION VS EXIT GAS O2 CONCENTRATION FOR PELLETS

Sulfur Dioxide Concentration

The question here is whether sulfuric acid emissions are directly proportional to the SO_2 level in the engine-out exhaust gas. If they are directly proportional to exhaust gas SO_2 level, this in-turn would

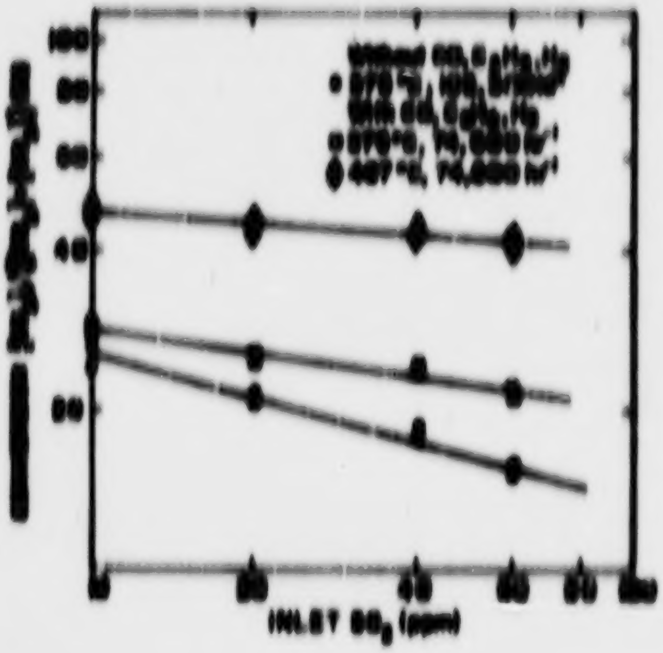
Figure 4-9

Effect of Other Exhaust Gases on SO_2 Oxidation



imply that sulfuric acid emissions for a given system would be directly proportional to the sulfur level of the fuel. Experimental evidence appears to indicate that sulfuric acid emissions are approximately proportional to the SO_2 level. Figure 4-10 contains data reported by Ford that show the conversion rate to be fairly level at widely varying SO_2 levels.

Figure 4-10
Effect of SO_2 Concentration on
SO_2 Oxidation



SECTION 5

HOW MUCH SULFURIC ACID DO CURRENT VEHICLES EMIT?

5.1 Sulfuric Acid Emissions from Non-Catalyst Vehicles

This section discusses the available sulfuric acid emission data for conventional non-catalyst vehicles. Sulfuric acid emissions from non-conventional non-catalyst vehicles such as stratified charge, Diesel, and lean burn vehicles are discussed in Section 8.

Work done in 1971 using the absorption method (EPA Stationary Source Method 8) indicated that non-catalyst cars emitted significant quantities of sulfuric acid (i.e. 10-20% conversion of fuel sulfur to sulfuric acid). Further work showed this measurement method to be unreliable in that sulfuric acid formation occurred in the measurement apparatus itself.

Work done in 1973 and later using the dilution tunnel method indicates that non-catalyst cars form about 1 mgpm of sulfuric acid when burning 0.03 weight % sulfur in the gasoline. Both Ford and Chrysler reported sulfuric acid data for conventional non-catalyst cars in their current and previous submissions to EPA. While General Motors reported no sulfuric acid data for conventional non-catalyst cars in their current submission to EPA, their previous submissions contained extensive data in this area.

The available data base is summarized in Table 5-1.

The results in this table shows sulfuric acid emissions of about 1 mgpm, on the average, but with numbers frequently higher with a maximum value of 5 mgpm. More recent data tend to be lower (i.e. under 1 mgpm). The above data indicate that conventional non-catalyst cars can emit over 1 mgpm.

TABLE 5-1. SULFATE EMISSIONS FROM CONVENTIONAL NON-CATALYST VEHICLES

Vehicle	Data Source	Test Cycle	Fuel Sulfur wt. %	Conversion to Sulfuric Acid	Sulfuric acid Emissions, mg/mi	No. of Tests	Sulfuric acid Emissions Normalized to 0.03% Fuel Sulfur, mg/mi
1972 Vehicle	[illegible] 5-30-74	1972 FTP	0.06	2.8	7	1	6
		40 mph 40 mph 40 mph	0.067 0.067 0.067	.2 .1 .2	.6 .6 .9	1 1 1	.2 .2 .2
Conventional Non-Catalyst Vehicles	GM 5-7-74	1972 FTPs					
1973 Pontiac			0.032	0.3	1	1	1
1973 Buick (Air)			0.036	0.8	<1	1	<0.9
1973 Chev. (Air)			0.15	0.1	1	1	.2
1972 Chev. (Air)			0.015	0.6	1	1	2
1973 Chev. (Air) Two Vehicle			0.05	2.6	9	1	5.6
1974 Ford Bench Engine	[illegible]	Hot Start FTP	0.033	–	2.7	3	2.7
		Cold Start FTP	0.033	–	2.6	3	2.6

TABLE 5-1 [illegible] (continued)

Vehicle	Data Source	Test Cycle	Fuel Sulfur wt.%	[illegible]	Sulfuric Acid Emissions, [illegible]	No. of Tests	[illegible]
		30 mph	[illegible]	—	[illegible]	2	[illegible]
		[illegible]	[illegible]	—	[illegible]	2	[illegible]
		[illegible]	[illegible]	—	[illegible]	2	[illegible]
		[illegible]	[illegible]	—	[illegible]	2	[illegible]
		[illegible]	[illegible]	—	[illegible]	2	[illegible]
		[illegible]	[illegible]	—	[illegible]	2	[illegible]
		FTP	[illegible]	—	[illegible]	2	[illegible]
		[illegible]	[illegible]	—	[illegible]	2	[illegible]
[illegible]	[illegible]						
	[illegible]	60 mph	[illegible]	—	1.4	2	1.2
		30 mph	[illegible]	—	[illegible]	2	[illegible]
		[illegible]	[illegible]	—	[illegible]	2	[illegible]
Chrysler	Chrysler	60 mph	[illegible]	—	[illegible]	1	[illegible]
Car [illegible]	[illegible]	60 mph	[illegible]	—	[illegible]	1	[illegible]
Chrysler	Chrysler	55 mph	[illegible]				
Car [illegible]	[illegible]			—	[illegible]	1	[illegible]
		[illegible]	[illegible]	—	[illegible]	1	[illegible]
		[illegible]	[illegible]	—	[illegible]	1	[illegible]
		[illegible]	[illegible]	—	[illegible]	1	[illegible]
		[illegible]	[illegible]		[illegible]	1	[illegible]
		[illegible]	[illegible]		[illegible]	[illegible]	[illegible]
		60 mph	[illegible]	—	[illegible]	11	[illegible]
[illegible]	[illegible]	FTP	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		FTP	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		FTP	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		FTP	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		FTP	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		FTP	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		FTP	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 5-1. SULFATE EMISSIONS FROM CONVENTIONAL NON-CATALYST VEHICLES (continued)

Vehicle	Data Source	Test Cycle	Fuel Sulfur wt. %	Conversion to Sulfuric Acid	Sulfuric Acid Emissions, mg/mi	No. of Tests	Sulfuric Acid Emissions Normalized to 0.03% Fuel Sulfur, mg/mi
		FTP	[illegible]	1.2	1.2	5	1.0
1974 Sedan	Ford 6-75	60 mph	[illegible]	—	.30	2	.30
		60	[illegible]	—	.14	2	.13
		60	[illegible]	—	.16	2	.17
		60	[illegible]	—	.16	2	.17
		60	[illegible]	—	.25	2	.23

5.2 Sulfuric Acid Emissions from Catalyst Vehicles

Conventional oxidation catalyst vehicles can emit substantially greater quantities of sulfuric acid than non-catalyst vehicles. Both monolithic and pelleted catalyst vehicles emit sulfuric acid. Determining emission factors for monolithic catalyst vehicles is relatively simple. However, the problems caused by the storage and release of sulfuric acid are more pronounced with pelleted catalysts. This phenomenon, which is explained in more detail in Section 5.2.2, makes it more complicated to determine sulfuric acid emission factors for pelleted catalysts. The emission data reported to EPA for catalyst vehicles is summarized in the next two sections.

5.2.1 Sulfuric Acid Emissions from Monolith Catalyst Vehicles

Sulfuric acid testing for monolith catalyst vehicles has been done by EPA, EPA contractors, Ford, Chrysler, GM, Nissan, and Engelhard. While most of the testing has been done on vehicles with air pumps, some limited testing has been done on vehicles without air pumps.

The most extensive testing of monolith catalyst vehicles without air pumps was done by Exxon Research and Engineering (Exxon) under EPA contract. Exxon tested two 1975 certification cars designed to meet the 1.5 HC, 15 CO, 3.1 NOx levels. These vehicles were tested as part of the EPA sulfuric acid test procedure development program. Under all test conditions sulfuric acid emissions were extremely low, at about 1 mgpm. Exxon also tested a rental Plymouth to verify that production cars had similar emissions to the certification cars. This car also had very low sulfuric acid emissions. The low sulfuric acid emissions can be attributed to the lack of an air pump with resultant low exhaust oxygen levels. The emission data for these vehicles is summarized in Table 5-2.

Table 5-2
EPA-Exxon Data for Plymouths
(0.03% Sulfur Fuel)
(1.4% O_2 in exhaust at 60 MPH)

Test Condition	Number of Tests	HC gpm	CO gpm	NOx gpm	H_2SO_4 mgpm
FTP	9	.19	4.2	2.7	1.5
FTP	8	.30	4.5	2.9	1.8
SC-7	5	.06	.72	1.6	.2
SC-7	5	.08	1.1	1.3	.06
FTP	1	.12	4.3	3.4	0
SC-7	5	.06	1.6	2.6	0

Engelhard reported two tests run on a Ford vehicle with the air pump disconnected. The results of these tests show about 2 mgpm sulfuric acid over the FTP. Since the FTP frequently gives lower sulfuric acid emissions than other test cycles, the Engelhard tests by themselves are somewhat inconclusive.

EPA test results indicate that low oxygen levels over the catalyst result in low sulfuric acid emissions. The potential of low oxygen levels as a sulfuric acid control technique is discussed in more detail in Section 7.

Sulfuric acid emissions from monolith catalyst vehicles with air injection are generally much higher than for those cars without air injection. EPA, Ford, and Chrysler have tested several cars of this type for sulfuric acid. One vehicle with a monolith catalyst and without air injection has been reported as having sulfuric acid emissions as high as 25 mpg over the SC7. This is apparently due to excess oxygen in the exhaust from lean carburetion.

Table 5-3
EPA Tests of Ford Certification Vehicles
(0.03% fuel sulfur)

Vehicle	Test Cycle	Number of Tests	HC gpm	CO gpm	NOx gpm	H_2SO_4 mgpm
Granada	Repetitive FETs	9	.31	.52	1.8	10.7
	Repetitive SC-7s	about 17	.30	1.2	1.6	18.8
	Repetitive SC-7s	30	.38	1.0	1.4	10.6
	FTP	8	.80	6.9	1.8	5.3
	SC-7 preceded by FTP	3	.31	1.5	1.6	20.6
	SC-7 preceded by FET	3	.33	1.8	1.8	20.0
	Duplicate SC-7 preceded by 2 FETs and 1 FTP	8				23.7
	Duplicate FETs preceded by 1 FTP and 2 SC-7s	8				30.7
Monarch	Repetitive SC7s	15	.28	2.1	1.3	15.3
	FTP	9	.65	6.3	1.3	3.5
	SC-7 preceded by FTP	3	.31	2.3	1.2	20.8
	SC-7 preceded by FET	3	.26	1.9	1.3	18.3
	Duplicate SC-7 preceded by 3 FETs and 1 FTP	5				23.2
	Duplicate FETs preceded by 1 FTP and 2 SC-7s	5				30.5
Maverick	Repetitive SC-7s	18	.13	.37	2.0	8.8
	Repetitive SC-7s	5	.13	1.2	.8	5.5
	Repetitive FETs	9	.11	.08	1.8	56

Table 3-4

Sulfuric Acid Emissions for Chrysler Vehicles

Car	Test Cycle	Preconditioning	Sulfuric Acid, mg/mi
Car [illegible] ([illegible] Sulfur Fuel)	60 mph 1 hour	60 mph 30 min.	97
	60 mph 1 hour	60 mph 2 hours	85
	60 mph 1 hour	70 mph 2 hours	89
	60 mph 1 hour	60 mph 4 hours	91
	60 mph 1 hour	60 mph 2 hours	105
	60 mph 1 hour	60 mph 4 hours	104
	60 mph 1 hour	60 mph 2 hours	111
	60 mph 1 hour	60 mph 4 hours	107
	60 mph 1 hour	60 mph 2 hours	95
	60 mph 1 hour	60 mph 4 hours	100
	60 mph 1 hour	60 mph 2 hours	98
	60 mph 1 hour	60 mph 4 hours	101
	60 mph 5 min.	60 mph 2 hours	93
	60 mph 10 min.	60 mph 2 hours	90
	60 mph 20 min	60 mph 2 hours	91
	60 mph 40 min	60 mph 2 hours	91
	60 mph 5 min.	60 mph 2 hours	91
	60 mph 10 min.	60 mph 2 hours	91
	60 mph 10 min.	60 mph 2 hours	108
	60 mph 40 min	60 mph 2 hours	91
	SC-7	5 SC-7s	6
	SC-7	2 SC-7s	4
	SC-7	5 SC-7s	3
	SC-7	2 SC-7	6
	SC-7	1 SC-7	6
	SC-7	5 SC-7s	28

Table 5-4
(Continued)

Car	Test Cycle	Pre-conditioning	Sulfuric Acid mg/mi
	SC-7	3 SC-7s	22
	SC-7	7 SC-7s	18
	SC-7	50 mph 1 hour	40
	SC-7	50 mph 1 hour and 3 SC-7s	31
Car 510 (0.031% Sulfur Fuel)	SC-7	1 SC-7	14
	SC-7	3 SC-7s	17
	SC-7	1 SC-7	19
	SC-7	3 SC-7s	9
	SC-7	5 SC-7s	8
	SC-7	1 SC-7	7
	SC-7	3 SC-7s	6
	SC-7	5 SC-7s	3
	SC-7	1 SC-7	16
	SC-7	3 SC-7s	17
	SC-7	7 SC-7s	38
	[illegible]		40

The FTP emissions for these two cars are as follows:

	HC	CO	NOx gpm
Car 607	.53	9.1	1.21
Car 510	.40	5.52	1.53

EPA-ECTD tested two 1975 Ford certification vehicles designed to meet the California and Federal standards (i.e. 50 state vehicles). These vehicles, a Granada and Monarch, were tested in the sulfuric acid test procedure development program. Also, a Ford Maverick certification vehicle designed to meet 1.5 HC, 15 CO, 3.1 NOx was tested in this program by EPA-ECTD and EPA-ORD. The results of these tests are given in Table 5-3.

EPA-ORD ran some limited tests on two Ford rental cars, a Granada and a Torino. The tests run were repetitive sulfate cycles which show sulfuric acid emissions from 5 to 25 mgpm.

Chrysler ran sulfuric acid tests on a monolith catalyst vehicle equipped with air injection and designed to meet 0.9 HC, 9.0 CO, 2.0 NOx (car 467). This vehicle gave about 100 mgpm sulfuric acid at 60 SS. Sulfuric acid emissions were lower but more variable over the sulfate cycle ranging from 3-49 mgpm. The emission values for both cars 518 and 467 are given in Table 5-4.

Ford Motor Company did their initial work with Battelle Labs with an engine dynamometer. An Engelhard catalyst equipped with air injection gave about 50 mgpm of sulfuric acid with 0.032 sulfur fuel at 60 mph. A GM pelleted catalyst with air injection showed similar results. Further work at Battelle through the CRC-APRAC CAPE 19 project concentrated on measuring sulfuric acid emissions from a 1975 351 CID Ford Torino. This work also showed about 50 mgpm of sulfuric acid at 60 mph.

Ford is also conducting a program at Southwest Research which, in part, will obtain emission factors for two 1975 Ford vehicles produced to meet the California standards. The two vehicles are a Pinto (5P13) and a 400 CID Torino (53A30) with monolith catalysts and air injection.

Table 5-5

Sulfuric Acid Emission Data for Ford Vehicles 0.032% Sulfur Fuel

Vehicle	Test	Number of Tests	Preconditioning	Sulfuric Acid, mgpm
Torino	60 mph	2	30 miles at 60 mph	55.5
	60 mph	2	130 miles at 60 mph	52.8
	60 mph	2	30 miles at 60 mph	28.0
	60 mph	2	30 miles at 60 mph	37.5
	60 mph	2	30 miles at 60 mph	45.9
	30 mph	2	170 miles at 60 mph	65.8
	30 mph	2	170 miles at 60 mph and 75 miles at 30 mph	78.7
	RC-1	2	105 miles @ 30 mph 2 RC-1s	24.2
	RC-1	2	105 miles at 30 mph and 7 RC-1s	33.5
	RC-1	2	1 RC-1	18.5
	RC-1	6	3 RC-1s	11.3
	RC-7	2	70 miles at 60 mph	23.4
	RC-7	2	70 miles at 60 mph and 1 RC-7	22.7
	RC-7	2	70 miles at 60 mph and 1 RC-7	36.2
	FTP	1	7 RC-7s and 1 FTP	37.6
	3 FETs	2	3 FTPs (hot start) and 1 FET	62.8
Pinto	60 mph	2	30 miles at 60 mph	24.1
	60 mph	2	130 miles at 60 mph	15.0
	60 mph	2	30 miles at 60 mph	10.5
	60 mph	2	30 miles at 60 mph	17.8

Table [illegible]
(continued)

Vehicle	Test	Number of Tests	Preconditioning	Sulfuric Acid, mg/mi
	60 mph	[illegible]	50 miles at 60 mph	17.1
	50 mph	[illegible]	170 miles at 60 mph	46.0
	50 mph	[illegible]	170 miles at 60 mph and 75 miles at 50 mph	56.4
	SC-1	[illegible]	100 miles at 50 mph and 7 SC-1s	13.3
	SC-1	[illegible]	7 SC-1s	18.3
	SC-7	[illegible]	70 miles at 60 mph	10.7
	SC-7	[illegible]	70 miles at 60 mph and 1 SC-7	10.8
	SC-7	[illegible]	70 miles at 60 mph and 1 SC-7	9.7
	FTP	1	7 SC-7s and 1 FTP	8.0
	3 FETs	[illegible]	3 FTPs (hot start) and 1 FET	13.1

The vehicles were run on the modified AMA cycle for [illegible] miles at the start of the program. The vehicles were then tested for sulfuric acid emissions at 60 mph, at 30 mph, over the FTP, and over SC-1 and SC-[illegible] and SC-7. Sulfuric acid emissions were about [illegible] mgpm and 10 mgpm for the Torino and Pinto respectively. Detailed data for these cars are given in Table 5-5.

5.2.3 Sulfuric Acid Emissions from Pelleted Catalyst Vehicles

Sulfate Storage and Release

Pelleted catalysts consist of about 2500 grams of alumina pellets with a noble metal coating. By contrast, a monolith contains about 100 grams of washcoat alumina with noble metal coating on an inert non-reactive cordierite support. The alumina, which is chemically basic, can react with the sulfuric acid produced by the catalyst to form aluminum sulfate and possibly aluminum sulfite. This reaction occurs at lower catalyst temperatures (e.g. 400°F) associated with lower speed operation. However, the reaction is reversible at higher catalyst temperatures associated with higher speed operation. The aluminum sulfate will decompose back to alumina and either SO_2 or SO_3. While it is not clear how much SO_2 versus SO_3 is formed from this decomposition, SO_2 that would be formed might be oxidized to SO_3 by the catalyst. The SO_3 may then form sulfuric acid by combining with water. Therefore the decomposition of aluminum sulfate could result in the sulfuric acid emissions.

At low speed operations when sulfuric acid can be stored, the vehicle would emit only small quantities of sulfuric acid. At higher speeds, great quantities of sulfuric acid can be emitted for temporary periods until the catalyst stabilizes. This storage and release mechanism can occur many times over the life of a catalyst. A short period of operation at 60 mph can release most of the stored sulfate allowing the catalyst to store sulfates once again during subsequent lower speed operation.

The type of prior driving will have a great effect on the level of sulfuric acid emissions obtained during a sulfuric acid test.

For example, operation of a vehicle over the FTP, a low speed cycle, generally results in storage relative to higher speed cycles. Even the SC-7 itself, with an average speed of 35 mph, can result in storage relative to a higher speed condition such as the FET. The storage-release phenomenon can introduce a large amount of variability in sulfuric acid emission results for pelleted catalysts.

Sulfuric Acid from Pelleted Catalysts Without Air Injection

EPA-ORD did extensive testing of two GM certification vehicles with pelleted catalysts but no air injection. These vehicles were designed to meet 1.5 HC, 15.0 CO, 3.1 NOx. These vehicles emitted small quantities of sulfuric acid, about 1 mgpm over the SC-7 cycle. The results of the EPA-ORD tests are summarized in Table 5-6.

Table 5-6
EPA Tests of GM Cars

Car	Test	Number of Tests	HC gpm	CO gpm	NOx gpm	H_2SO_4 mgpm
Impala (Car 083OR)	Repetitive SC-7's	7	.61	26.8	1.0	1.3
	FTP	9	.41	5.1	1.0	.5
Chevelle	Repetitive SC-7's	6	.40	12.6	4.2	.6
	FTP	8	.60	12.0	3.0	.6

EPA-NERC tested three pelleted catalyst cars without air injection

(1) 1975 Chevrolet 350 CID production car supplied by GM

(2) 1975 Chevrolet 350 CID Certification car (Car 0A308) supplied by GM and also tested by EPA-ORD

(3) 1975 Chevrolet Rental Vehicle

About 1,000 miles of preconditioning at 30 mph with 0.032 sulfur fuel was run on the first car to stabilize the catalyst. During this time, sulfuric acid emissions rose to a maximum stable value of 8 mgpm. After this, 24 sulfuric acid cycles were run with the first cycle showing sulfuric acid emissions of 64 mgpm. The rapid decline of sulfate emissions with time can be seen in Table 5-7. Apparently, significant sulfate storage occurred over the 1,000 miles at 30 mph. The vehicle quickly stabilized to show sulfuric acid emissions of about 1 mgpm. The car was then tested at 60 mph and showed sulfuric acid emissions of about 35 mgpm.

The second two vehicles were tested only on sulfuric acid cycles and showed sulfuric acid emissions of about 1 mgpm. Table 5-7 lists the sulfuric acid emissions obtained in the order the tests were run for all three vehicles.

GM has run a number of vehicles without air injection including cars that meet both the Federal and the California standards for 1975. Two of the cars were 1975 Chevrolets and were tested over the FTP, HWFET, SC, and some steady state speeds. The third car (R5451) is a Buick designed to meet the 1975 California standards of 0.9 HC, 9.0 CO, 2.0 NOx. All three cars had low sulfuric acid emissions, generally below 10 mgpm. This is especially significant for the Buick which meets the stricter California standards. One Chevrolet had much higher sulfuric acid emissions (50 mgpm) at a 60 mph steady state.

Table 5-7

Sulfuric Acid Emissions for GM Cars
0.03% Fuel Sulfur

Car	Test	Number of Tests	Sulfuric Acid mg/mi
1975 Chevrolet Production Car	SC-1	5	.4
	30 mph for 1,000 miles	29	8 stable value
	SC-1	1	64
	SC-1	1	25
	SC-1	1	11
	SC-1	1	6
	SC-1	1	5
	SC-1	1	3
	SC-1	1	3
	SC-1	1	2
	SC-1	1	2
	SC-3	8	1
	SC-2	6	1
	FTP	2	.4
	SC-1	4	1
	FET	2	6
	60 mph	6	15
1975 Chevrolet Emission data car	SC-1	5	1
1975 Chevrolet Rental Car	SC-1	4	1

The sulfuric acid emissions for these three vehicles are listed in Table 5-8. The gaseous emissions for these three cars over the FTP are given in Table 5-9.

With Air Injection

Pelleted catalysts with air injection tend to give higher sulfuric acid values than pelleted catalysts without air injection. Most of the tests on pelleted catalysts with air injection were run by EPA and GM.

EPA tests were run on two AMC Hornets and with the GM 160 in.^{3} pelleted catalyst with air injection. Both cars were identical 1975 production cars run on modified AMA mileage accumulation. The tests were done under an EPA contract with Southwest Research Institute. These cars showed sulfuric acid emissions ranging from about 30 to 60 mgpm with most of the values about 50 mgpm. The emissions obtained by Southwest on these cars are listed in Table 5-10.

Exxon ran some very limited tests on an AMC Matador rental vehicle equipped with a pelleted catalyst and air injection. The car was run on HC-7 without any preconditioning. The sulfuric acid emissions obtained were very low as shown in Table 5-11.

Table 5-11
Exxon Test on AMC Matador
Pelleted Catalyst with Air Injection

Test	HC gpm	CO gpm	NOx gpm	H_2SO_4 mgpm
HC-7 (10 times)	.1	.36	2.0	1.7
FTP	.28	.96	2.1	.8

Table 5-8

Sulfuric Acid Emissions for GM Cars (normalized to 0.03% sulfur fuel)

Car	Test	Number of Tests	Sulfuric Acid mgpm
Chevrolet 85501 (6,000 miles)	S-1	3	12
	40 mph	6	10
	FET	6	15
	55 mph	5	12
Buick 85451 (2,000 miles)	FTP	7	1
	FET	8	10
	60 mph	6	10
Chevrolet 85948 (1,200 miles)	FTP	3	0
	30mph	4	8
	40mph	4	50
	S-7	4	8
	50mph	4	8

Table 5-9

Gaseous FTP Emissions for GM Cars

Car	HC	CO	NO_x gpm
Chevrolet (R5501)	.54	5.90	3.06
Buick (R1451)	.66	3.39	1.65
Chevrolet (R 5948)	.69	10.53	1.90

Table 5-10
Southwest Research Tests
of AMC Pelleted Catalyst
Vehicles with Air Injection

Car	Test	Number of Tests	HC gpm	CO gpm	NO_x gpm	H_2SO_4 mg/mi
Hornet [illegible]	FTPs	9	.6	6.1	2.7	10.8
	Repetitive SC-7s	10	.1	.2	2.4	57
	Repetitive SC-9s	12	.1	.1	2.3	60
	Repetitive SC-7s	12	.1	.1	2.2	56
	SC-7 Preceded by FTP	3	.1	.1	2.6	51
	SC-7 Preceded by PDT	3	.1	.2	2.3	51
Hornet [illegible]	FTPs	9	.6	4.7	2.9	20
	Repetitive SC-7	10	.1	.2	2.6	54
	SC-7 Preceded by FTP	3	.1	.1	2.3	52
	SC-7 Preceded by PDT	3	.1	.1	2.4	67

It was noted that low amounts of SO_3 were recovered during these tests indicating the catalyst was probably storing. It is therefore impossible to make any valid conclusions from this brief test other than to note the need for adequate preconditioning.

GM has extensively tested six pelleted catalyst vehicles with air injection designed to meet the California standards. These cars and their gaseous emissions over the FTP are listed in Table 5-12. These cars were tested for sulfuric acid over various test cycles. The emissions were as high as 130 mgpm at 60 SS and are listed in Table 5-13 normalized to 0.03% fuel sulfur. The tests were run in the order shown in the table.

Ford and Chrysler have each done some limited testing of pelleted catalysts.

Ford tested a 1976 Ford LTD equipped with a GM 260 in^3 pelleted catalyst. The vehicle was calibrated to meet the California standards and gave stable sulfuric acid emissions of about 60 mgpm over SC-7 with 0.03% fuel sulfur. These values are in agreement with earlier Ford work on an engine dynamometer at Battelle which found a pelleted catalyst with air injection to emit about 50 mgpm.

Chrysler tested a pelleted catalyst on one of their cars with air injection (car 384). They found this car gave essentially the same sulfuric acid emissions as car 467 which was similar to car 384 except it had a monolith catalyst. Car 467 emitted about 100 mgpm over SC-7 with 0.03% sulfur fuel.

Table 5-18
GM Tests of
Gaseous Emissions

Car	HC	CO	NO_x
(1) 350 CID Fuel injection 1975 Calif. Vehicle	--	--	--
(2) 1975 Cadillac production vehicle	---	---	---
(3) 1975 350-4 Nova production vehicle	---	---	---
(4) 350-2 1974 Chev. (S 5036)	.75	6.67	2.10
(5) 350-2 1975 Chevrolet (B-5052)	.60	9.00	1.63
(6) 350-2 1975 Chevrolet (B-5049)	.55	7.63	1.76

Table 5-11
Sulfuric Acid Emissions for GM Cars with Air Injection

Vehicle	Test	Number of Tests	Sulfuric Acid mgpm
(1) Fuel Injection Car	Repetitive AC-7a	12	10
(2) Cadillac	Repetitive AC-7a	8	35
	Repetitive AC-7a	7	40
	Repetitive AC-7a	7	50
(3) Chevrolet Nova	FTP	10	10
	AC-7	10	25
	FET	10	40
(4) Chevrolet (B5050)	FET	4	7
	20 mph	4	40
	FTP	4	8
	30 mph	4	30
	40 mph	6	70
	AC-1	5	80
	50 mph	4	90
	FET	4	100
	60 mph	4	120
(5) Chevrolet (B5052)	FTP	3	20
	30 mph	4	70
	40 mph	4	80
	AC-1	4	50
	FET	4	60
	55 mph	4	90
	50 mph	4	8

Table 5-13 (continued)

Vehicle	Test	Number of Tests	Sulfuric Acid mgpm
(f) Chevrolet (B5069)	FTP	3	4
	30 mph	6	5
	40 mph	6	30
	RC-1	6	40
	50 mph	6	30
	FET	6	60
	60 mph	6	120

SECTION 6

HOW CAN SULFURIC ACID EMISSIONS FROM AUTOMOBILES BE CONTROLLED?

This section discusses both non-vehicle and vehicle approaches toward controlling sulfuric acid emissions. These approaches are applicable for both catalyst-equipped and non catalyst-equipped vehicles.

6.1 Fuel Desulfurization

There appears to be general agreement that, in the fuel sulfur ranges of interest, for the same systems, sulfuric acid emissions are directly proportional to the fuel sulfur level. Therefore, reducing the level of sulfur in the fuel will reduce sulfuric acid emissions. The subject of fuel desulfurization was one of the items covered in the EPA request for information published in the *Federal Register* of March 8, 1974. A summary of the comments from the respondents is shown below in Table 6-1.

Table 6-1
Some Costs for Fuel Desulfurization[1]

	Range	Median
Construction lead time	0 to 6 years	4 years
Capital investment	$2 to 12 billion	$3 1/2 billion
Annual operating costs	$12 to 200 million	$17 million
Cost per gallon of gasoline	0.5 to 2.0 cents per gallon	1 cent per gallon
Energy penalty	1/2 to 1 1/2%	1%
Gasoline yield penalty[2]	1 to 2%	1%

Note:

[1] 100 ppm sulfur

[2] At constant crude input

The estimates for fuel cost increments give information that can be used to compare the cost to the consumer of a system for controlling sulfuric acid emissions from the vehicle to the customer costs due to fuel desulfurization.

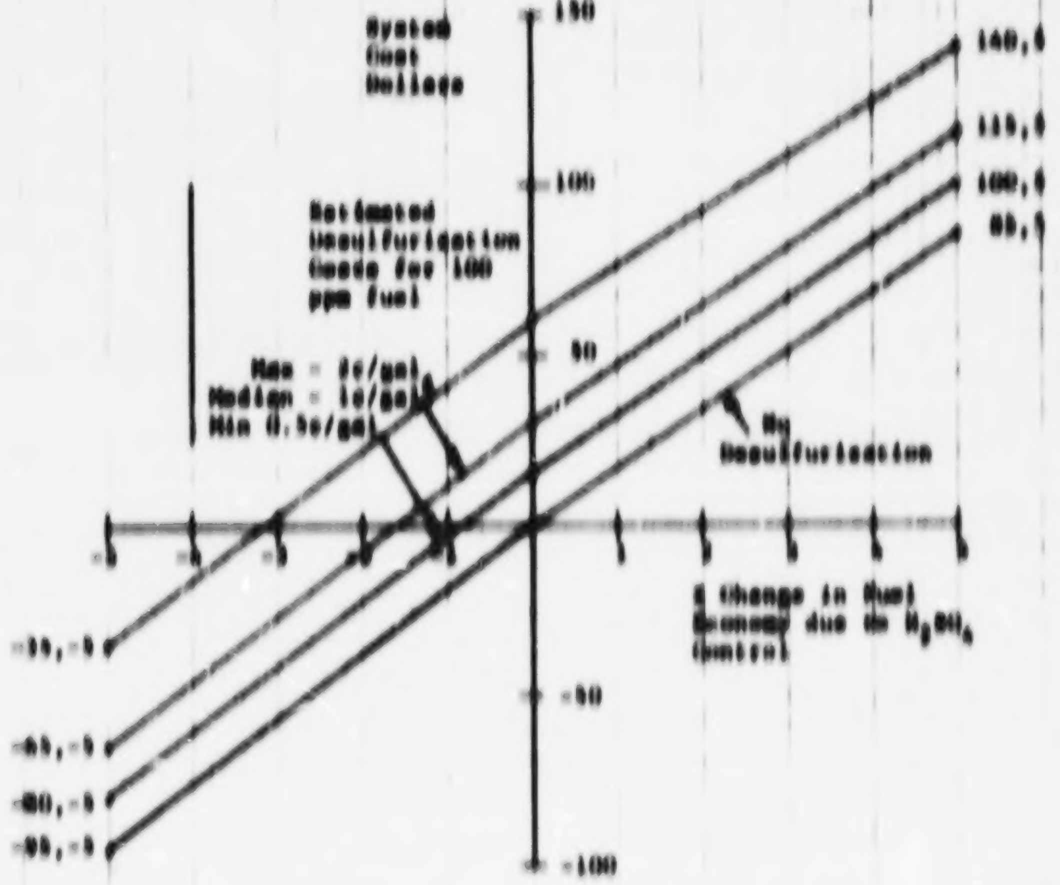
The assumptions for such a comparison were as follows: the customer costs for fuel for 50,000 miles of vehicle operation were calculated for the range and the median of the estimates using the average fuel economy of the 1976 models, MPG = 17.6. For 0.5, 1.0, and 2.0 cents per gallon, the additional costs are $14.20, $28.40, and $56.80 respectively. These values are rounded to $15, $30 and $60. If the system used to control sulfuric acid emissions would cost less than these values it would be advantageous to control sulfuric acid on the vehicle. If the sulfuric acid emission control systems were to cost more than these values, it would appear to be beneficial to the customer to have his fuel desulfurized. However, it should be emphasized that this comparison is simplistic and that no other implications (other than cost to consumer) were considered; e.g. imports of the refiner, capital investment capabilities, etc.

The impacts of sulfuric acid control technology on cost, including operating cost (fuel economy and maintenance costs), are not well known at this time. As an indication of what the range of impacts might be, the report team has calculated what the sulfuric acid emission control system could cost for the case given above modified by a plus and minus five percent fuel economy effect. The results are shown in Figure 6-1.

Figure 6-1 indicates that systems that cost more than the indicated amount will be more costly to the customer than desulfurizing the fuel. Also, Figure 6-1 shows that only a small (1 to 3 percent) fuel economy loss can be tolerated before the extra cost of fuel more than outweighs

Figure 6-1

Control System Costs to Just Equal Fuel Desulfurization Costs as a Function of H_2SO_4 Control Fuel Economy Effect



the cost of desulfurization to the customer. It must be kept in mind that maintenance costs were not included in the calculations for Figure 6-1. Again, it should be noted that Figure 6-1 is based only on consumer costs, e.g., if energy conservation also were a desired objective then Figure 6-1 would have to be modified.

Several qualifications concerning Figure 6-1 must be mentioned. The fuel desulfurization costs shown are for reducing the fuel sulfur level to 100 ppm, a 67 percent reduction. If more control, say to 30 ppm, is necessary the cost estimates are not well established, although they would be at the top end of the range, 3 cents per gallon. Figure 6-1 and the assumptions and calculations for it also do not consider the possibility of some desulfurization and some on-vehicle control. Such a strategy analysis is beyond the scope of this report. Figure 6-1 is not specific to any sulfuric acid emission control system, however, it does give ranges of system cost to compare specific systems against. Finally, apportioning the cost and fuel economy impacts to just sulfuric acid control is difficult to do as the following two cases indicate. First consider the control technique of dumping the air pump output to the atmosphere after the first few minutes of startup operation. It is possible that such an approach may cause a HC problem. If the spark is retarded and fuel economy suffers, is the fuel economy loss due to NO or H_2SO_4 control? If the 3-way catalyst approach is used and fuel injection is needed to keep the oxygen level in the proper region for H_2SO_4 control, and the fuel economy improves, to what is the fuel injection cost and fuel economy effect due: H_2SO_4 control or NO/CO/HC control?

In summary, it is the conclusion of this report that Figure 6-1 indicates that systems for controlling just sulfuric acid emissions alone that cost more than $30 should be examined carefully.

6.2 Fuel Additives

Theoretically, a material could be added to the fuel that would tie up the sulfur in the fuel or combine with the SO_2 formed to reduce the SO_2 available for oxidation to SO_3. Ideally the resultant products would be harmless and it would be attractive if the additive had anti-knock properties.

One candidate, though certainly not an ideal one, is tetraethyl lead.

The possibility of using leaded fuel as a means of reducing sulfuric acid emissions has been discussed by Chrysler Corporation. The lead in the fuel could tie up some of the fuel sulfur as lead sulfate which is insoluble and may have lesser health effects than sulfuric acid. However, there is insufficient lead in even low lead fuel (0.5 g/gal of lead) to tie up much of the sulfur. With 0.03% sulfur fuel, less than 10% of the fuel sulfur could be converted to lead sulfate with leaded fuel containing 0.5 g/gal lead.

Furthermore, standard oxidation catalysts are rapidly poisoned by leaded fuel. Some preliminary work by Chrysler indicates that ethylene dibromide (one of the two scavengers used with leaded fuel) poisons catalysts while lead or ethylene dichloride (the other scavenger used with leaded fuel) does not. Chrysler has also suggested that gasoline containing lead alone or lead and ethylene dichloride could be used with catalyst vehicles. However, both Ford and GM feel that lead alone does poison catalysts and cannot be used with catalyst cars. This report concludes that much more work is needed to establish if lead may be able to be used with conventional catalysts.

DuPont is developing a high temperature catalyst that may be resistant to lead poisoning. Leaded fuel used with this catalyst would not lower sulfates significantly by formation of lead sulfate. However, it is possible that this catalyst has lower activity for SO_2 oxidation than other catalysts or that lead selectively poisons this catalyst for SO_2 oxidation.

Other than tetraethyl lead, not much work has been done with fuel additives to either tie up fuel sulfur or to combine with SO_3. The report team considers that if additives to tie up fuel sulfur were available, they would probably already be used for fuel oil sulfur control. The use of a fuel additive that would tie up the SO_3 formed, likewise has received little attention because, in the opinion of the report team, in view of the work needed to find such an additive and to determine quantitatively its effects on engine wear and catalyst durability it is apparently not considered to be a promising approach. The determination of the effects of trace quantities of lead on catalyst durability, for example, was (and still is) a major program. With little to indicate that such an approach will work for sulfuric acid control, the researchers in the field probably consider other avenues to be more productive.

6.3 Combustion Modification

Modification of the combustion process was one of the first approaches tried toward controlling gaseous emissions. For example, leaning out of the air/fuel ratio to control HC and CO emissions and exhaust gas recirculation (EGR) to control NOx emissions have proved to be effective control measures. However, almost no real work has been tried in an attempt to control the formation of SO_3 in the engine. Apparently, most investigators consider it fruitless to try to prevent the oxidation of sulfur to SO_3 in the combustion chamber while maintaining the excellent combustion efficiency typical of the conventional engine. This report analysis tends to concur with this approach, however, it would be interesting to have data on the extent (if any) of SO_2 reduction due to combustion modifications.

Analogous to the case of fuel additives, an additive is not precluded for addition to the inlet air to the engine. EGR is one example, with CO_2 being the primary "air additive". One potential candidate for control of SO_2 emissions would be ammonia (NH_3) addition. Ammonium sulfate might be formed. The commercial process for making ammonium sulfate uses sulfuric acid and ammonia, not SO_2 and ammonia. However, several potential drawbacks with this approach are evident. First, NH_3 would most probably decompose to nitrogen and hydrogen at combustion temperature. Second, even if it did not decompose, NH_3 could be oxidized to NO increasing the NOx control task (particularly if an oxidation catalyst is used). Third, even if ammonium sulfate were formed it is not clear to the report team that this kind of emission is a harmless one. Fourth, the hardware and extra maintenance required to keep any sort of air additive system functioning on the vehicle implies higher customer costs. Finally, current sulfuric acid analysis techniques do not distinguish between sulfuric acid and ammonium sulfate, though they can be modified to detect such differences. Ammonia injection after the oxidation catalyst, though not a combustion modification, may be a technique to provide ammonia at a more useful location, but would be subject to the last three drawbacks which were previously mentioned.

Other additives for the inlet air stream would appear to have at least the same drawback as the fourth comment cited above for NH_3 addition.

The combustion modification approach does not appear to be too promising at this point in time, and it is understandable why little work was reported in this area.

SECTION 7

HOW CAN SULFURIC ACID EMISSIONS BE CONTROLLED FROM CATALYST AUTOMOBILES?

7.1 Oxidation Catalyst Systems

Oxidation catalysts have been criticized due to their role in the generation of sulfuric acid emissions. Often overlooked are the HC, and CO benefits provided by the catalyst and the engine calibration flexibility provided by catalysts which in turn provides for more optimal fuel economy. This is quite apparent in the 26.6% overall improvement in fuel economy of the 1976 models over the 1975 models.*

7.1.1 Oxidation Catalyst Modifications

Dramatic reductions of sulfuric acid emissions from catalyst modification have not been realized at this point in time. There are several reasons for this in the opinion of the report team: 1) final sulfuric acid testing procedures and sulfuric acid emission standards have not yet been established, 2) most auto manufacturers depend on suppliers for improvements in catalyst technology, 3) neither the manufacturers nor the catalyst suppliers have had sulfuric acid testing capabilities very long, and 4) the sulfuric acid emissions of present systems are not yet completely understood.

The following sections discuss catalyst parameters which have been investigated for sulfuric acid reduction potential. All HC, CO, and NOx emission values are from 1975 FTP tests and sulfuric acid emission values are from the test indicated in the table and are corrected to 0.030 wt% sulfur in the fuel.

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*T. C. Austin, R. B. Michael and G. R. Service, "Passenger Car Fuel Economy Trends Through 1976," SAE Paper 750957.

Type of active material

A few base metal catalysts have been examined for sulfuric acid emissions. Those tests are presented in Table 7-1. The base metal catalyst on the Ford vehicle demonstrated no improvements over noble metal catalysts, but the GM catalyst did. No firm conclusions about sulfuric acid emissions from base metal catalysts can be made from this data. In light of past durability problems (primarily sulfur tolerance problems) base metal catalysts alone do not appear to be the optimum solution in the near future. There is work going on, however, to utilize noble metal-promoted-base metals catalysts. These catalysts are primarily base metal, but have small amounts of noble metals added to improve their activity and poison tolerance.

Active metal composition

Various noble metals combinations which are currently used in oxidation catalysts have been examined for potential sulfuric acid emission reductions. These data are presented in Table 7-2. The only data which indicate that platinum/rhodium catalysts do not provide reduced sulfate emissions are from Johnson-Matthey (J-M), the parent company of Matthey-Bishop (M-B). The J-M data is not convincing since all data points are at extremely low levels of sulfuric acid emissions, but J-M's disagreement is significant since they have more production experience with Pt/Rh catalysts than any other catalyst manufacturer. M-B indicates that they are not certain, but they believe that differences in their substrate are responsible for lower sulfuric acid emissions. The data indicate no

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significant differences between all platinum (Pt) and platinum/palladium (Pt/Pd). More information will be provided by a current EPA contract with Exxon and future Ford studies.

Pt/Pd catalysts are said to have better light-off characteristics than all Pt catalysts. M-B indicates that all Pt catalysts have better durability than Pt/Rh catalysts as shown in Figure 7-1. Pt/Pd catalyst durability is said to be poorer than all Pt, but better than for Pt/Rh.

- Active metal loading

The only vehicle results available agree with earlier GM laboratory work in that they indicate only very small increases in sulfuric acid emissions for increases in noble metal loading. The increase in noble metal loading was about 60% in Pt/Pd for the pelleted catalyst. These results are presented in Figures 7-2* and 7-3*. Only Pt/Pd was used in these tests. These results need to be verified for Pt and Pt/Rh as well. Also the increased loading concept needs to be verified on the BC-7. This could be important as increased noble metal loadings are known to provide improved durability for HC and CO.

- Dispersion of active metal

Perovskite catalysts are being tested which contain the active metals in a lattice structure. DuPont has indicated that the perovskite catalysts have improved thermal stability which would enable them to be placed closer to the exhaust manifold. This could provide higher temperature operation for reduced sulfuric acid emissions and improved HC conversion efficiency. HC conversion has not been very high when operated at conventional temperatures for the perovskite oxidation catalysts. These

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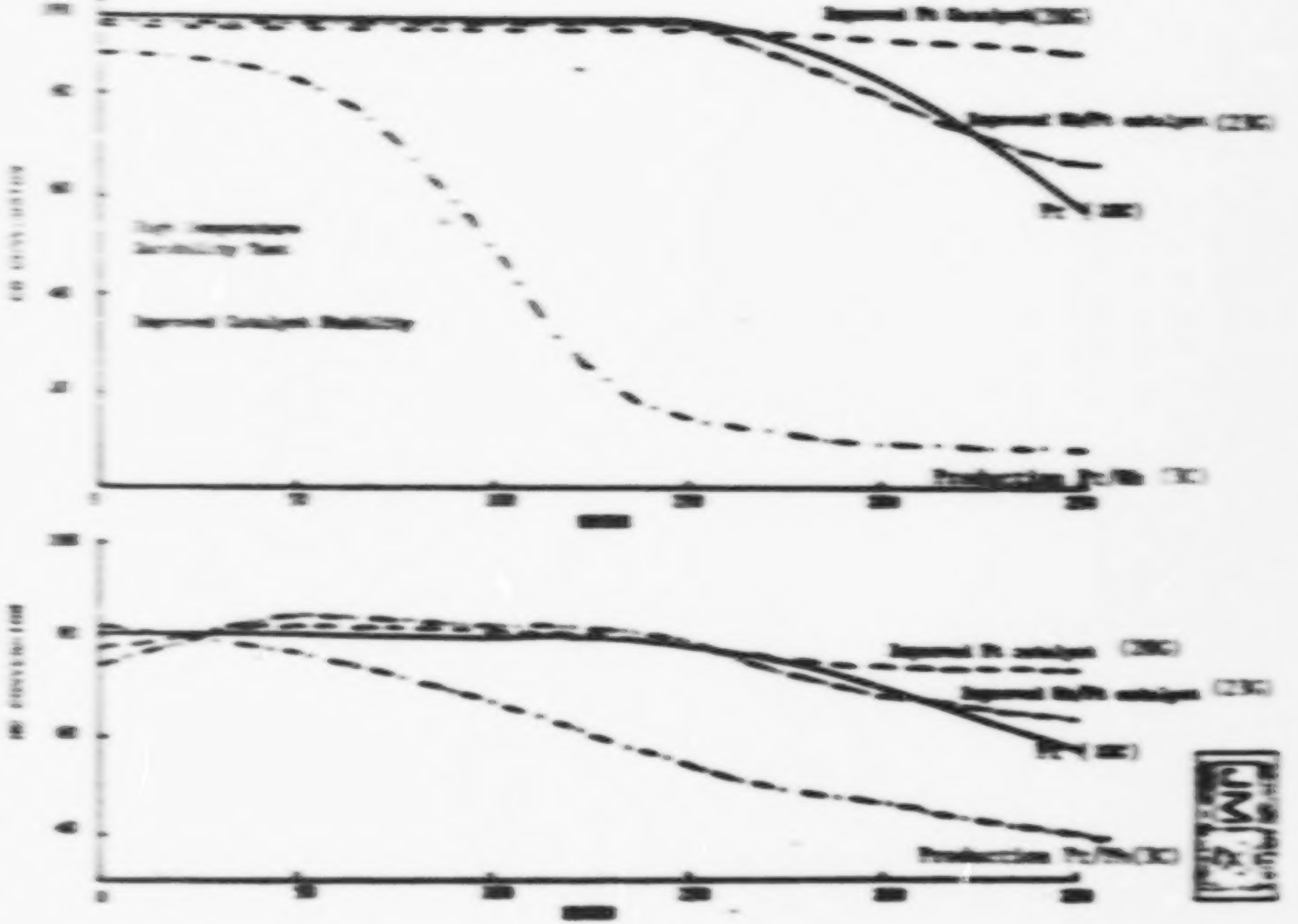
*E. L. Holt, K. C. Bachman, W. R. Leppard, E. E. Wigg, and J. H. Somers, "Control of Automotive Sulfate Emissions", SAE paper 750683.

Figure 7-1
Durability Results for Different Catalysts
(Ref. 7-7)



catalysts are also said to be chemically stable and could possibly tolerate operation with leaded fuels. This could potentially reduce sulfuric acid emissions also. No vehicle data on sulfuric acid emissions is available yet, but lab data from Chrysler indicates a 90% reduction as compared to conventional oxidation catalysts.

The effect of conventional dispersion, i.e., how the active sites are distributed on the catalyst, on sulfuric acid emissions has not been reported.

Catalyst volume and space velocity

Since space velocity is defined as the exhaust gas flow rate divided by the converter volume, space velocity and catalyst volume will be discussed together. Early laboratory test data had indicated that sulfuric acid emissions would increase as the catalyst volume increased (or space velocity decreased). The Exxon vehicle data presented in Figures 7-2, 7-3, 7-4, and 7-5 indicate a contrary result. There was generally no increase and even reductions of sulfuric acid emissions with increased catalyst volume. The two pelleted catalysts were 160 and 260 cubic inches respectively, and two monoliths were used in place of one to increase the volume. The Exxon tests were on 1975 FTP's and 60 SS so this effect can not automatically be assumed to be similar over the SC-7, but these initial tests were very encouraging. The effect of catalyst volume must be determined as this is an important parameter which can be used to recover possible losses in HC and CO control if exhaust oxygen levels are reduced to control sulfuric acid, if these initial Exxon results are found to be accurate.

This has become a very important issue to EPA as some vehicle manufacturers are now reducing catalyst volumes and making claims of sulfuric acid emission improvements - with no vehicle results to substantiate those claims. If the Exxon results are correct, then HC and

Figure 7-2

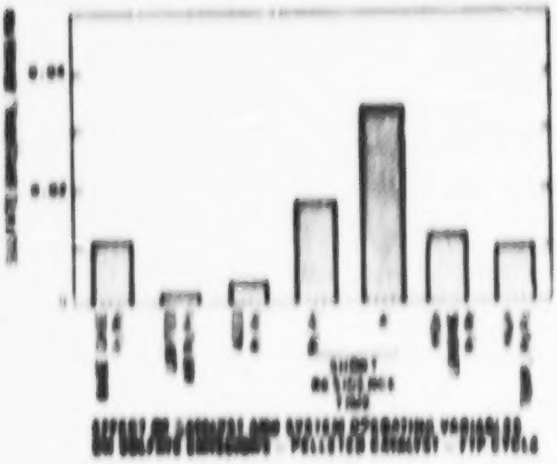


Figure 7-3

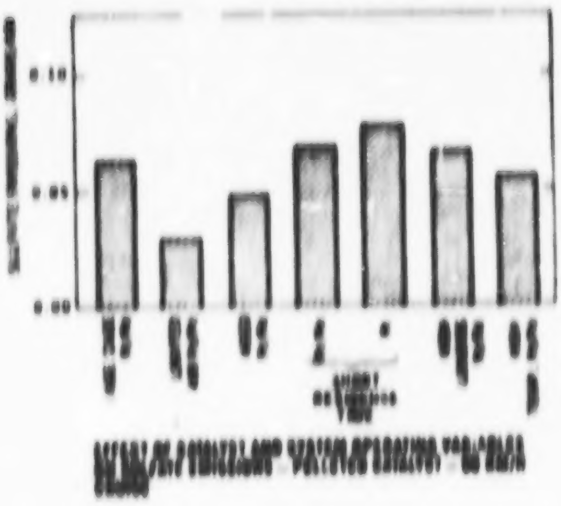


Figure 7-4

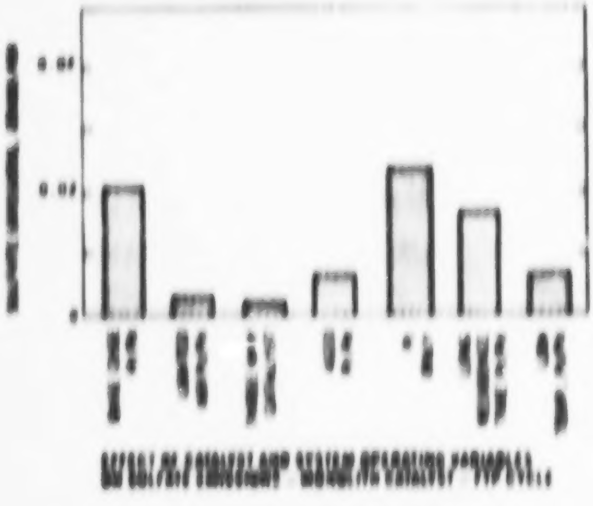
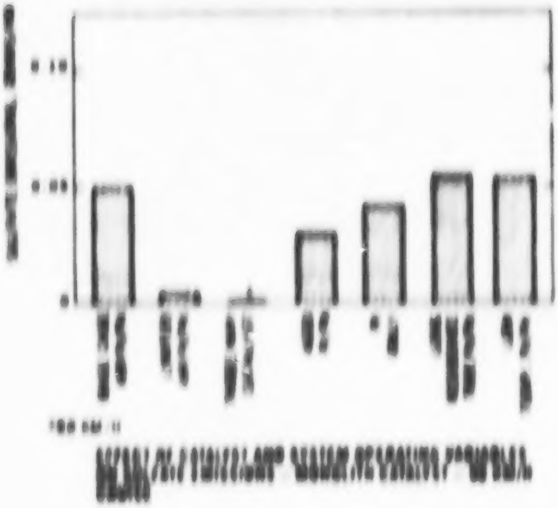


Figure 7-5



CO durability and emissions will possibly be degraded with no improvement in sulfuric acid emissions.

Catalyst parameters such as washcoat or pellet composition, preparation, and surface area have not been studied for effects on vehicle sulfuric acid emissions. These studies should probably be done by catalyst manufacturers, who have the most expertise in this area, although the automobile manufacturers have some capability, too. This is a good example of a possible cooperative catalyst development program between the auto makers and catalyst suppliers. No such program has been reported.

Selective poisoning of oxidation catalysts has been discussed by many manufacturers but only Chrysler reported work in this area. The Chrysler efforts consisted of brief lab testing which demonstrated about a 50% reduction in sulfuric acid with lead poisoning. In the same study, Chrysler also successfully heat aged two catalysts. Sulfuric acid reductions from heat aging were comparable to the results from selective poisoning. Changes in HC and CO efficiency were not reported. Since it is known that some catalysts used in the contact process for making sulfuric acid are poisoned by arsenic, the lack of any data from testing selective catalyst poisons is disappointing and a major area in which information is lacking.

Others have looked at the effects of catalyst aging in actual vehicle testing as in table 7-1. Only the VW testing used the same catalyst (as opposed to two identical catalysts - one relatively fresh and the other aged) for sulfuric acid testing during mileage accumulation. The results in table 7-1 are not sufficient to be absolutely conclusive, but the indication is that sulfuric acid emissions decrease with aging. This agrees with previous lab work and would be expected. As HC and CO

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oxidation deteriorates over mileage accumulation, SO_2 oxidation is assumed to deteriorate as well. This data would indicate that in a certification procedure the deterioration factor for sulfuric acid emissions would probably be a value of 1.0 for almost all vehicles if the sulfuric acid deterioration factor is calculated as currently done for HC, CO, and NOx. The Exxon fleet testing* of twenty 1975 California vehicles over 32,000 miles further supports this conclusion even though AMA mileage accumulation was not used in this study.

7.1.2 Modifications of Oxidation Catalyst Feedgases

It is the conclusion of this study that the primary sulfuric acid control technique that will be used in the near term to control sulfuric acid emissions will be modifications to the exhaust gases entering the oxidation catalyst. Oxygen level and temperature will be the primary control parameters.

- Oxygen level

Most investigators, with the possible exception of Ford, agree that control of the feedgas oxygen levels to the catalyst is the most important, controllable factor in the generation of sulfuric acid emissions. The data in Table 7-4 indicate the effects of low and high exhaust oxygen levels. Data at oxygen levels between these values have not been reported, but sulfuric acid emissions would be expected to be intermediate. To fully understand the oxygen levels in Table 7-4 it must be understood that at a stoichiometric A/F ratio the oxygen level of the exhaust into the catalyst is not zero as indicated by ideal combustion equations. As seen in Figure 7-6, the stoichiometric oxygen level may be as high as about 0.7%.

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*"Fleet Test of 20 1975 California Vehicles," Exxon Research and Engineering Company, October 8, 1975.

Table 7-[illegible]

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		1230					20
		1230					15
		1230					15
		900		.21	1.46		0.4
	[illegible]	671		.29	1.39		20
		1150	1.32				[illegible]
		1150					[illegible]
		1150					[illegible]
		1150					[illegible]
				.22	1.39		3
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							4
				.33	5.73		3
	[illegible]			.29	1.39		20
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				.29	1.39		[illegible]
[illegible]	[illegible]			.42	5.34	.67	1
	[illegible]			.38	3.27	.42	2
	[illegible]			.46	4.41	1.43	3

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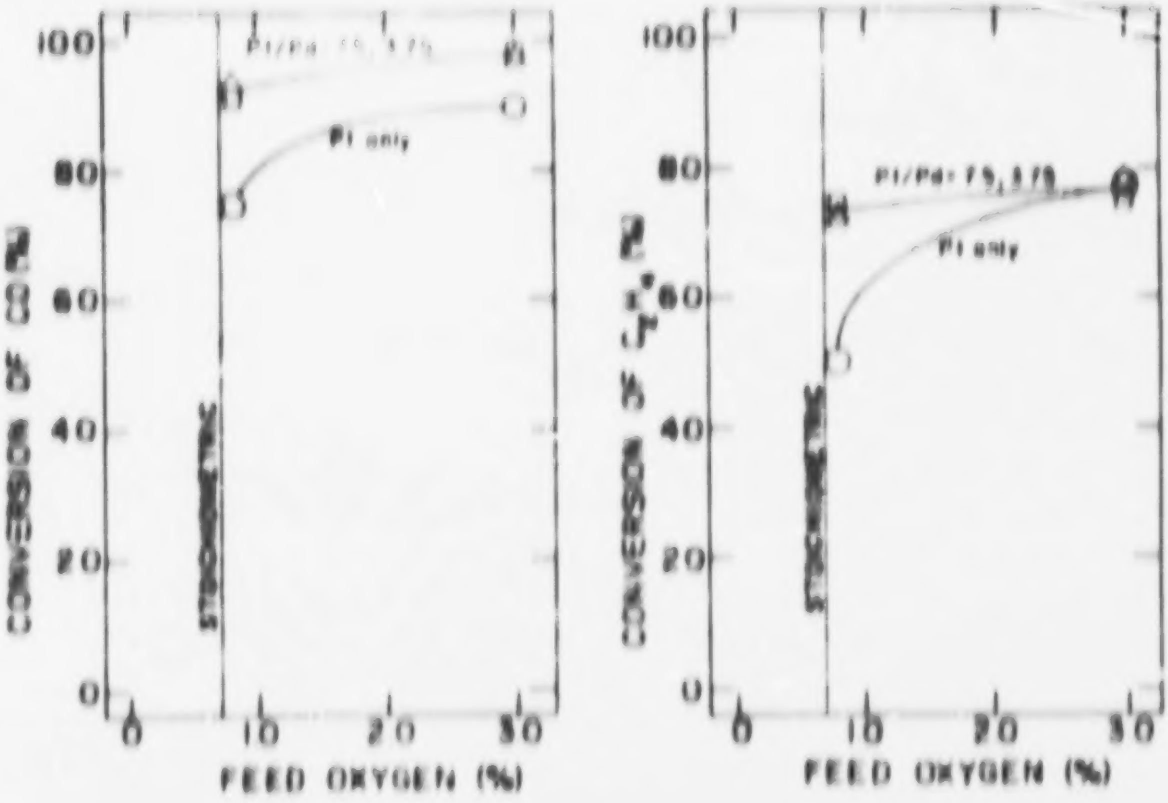
Figure 7-8

Conversion of CO and ethylene as a function of oxygen content for three engine aged catalysts evaluated on laboratory oxidation test unit.
VHSV = 40,000, 0.05 troy oz. PM/160 in³, Pt/Pd ratio as shown.
Inlet temperature 400°C.



There are several items of interest in Table 7-4. First the Exxon data indicate that by using air injection only during warm up, sulfuric acid emissions can be greatly reduced. Also of importance here are the greatly increased CO emissions for the monolithic catalyst vehicle without full AIR. This apparently is due to the large difference between active surface area and catalyst volume between the pelleted catalyst and the monolithic catalyst. The increased CO emissions point to the need for fuel metering improvements to accompany reduced oxygen levels at the .41 HC, 3.4 CO levels.

Also of interest are the Volkswagen and Exxon data which utilize both 3-way and oxidation catalysts. The sulfuric acid emissions from both types of catalysts are very low when oxygen levels are low. Thus there is no "magic" reason why 3-way catalysts have low sulfuric acid emissions, as oxidation catalysts can have low sulfuric acid emissions too at similar oxygen levels. In fact 3-way and oxidation catalyst formulations are not greatly different except that 3-way catalysts are specifically designed to operate at very low oxygen levels. Because of their design, 3-way catalysts offer better HC, CO, and NOx conversion efficiencies than oxidation catalysts at low exhaust oxygen levels. VW has already certified oxidation catalyst vehicles which depend on the oxidation catalyst for some NOx control. The GM data also indicate some NOx conversion at low oxygen levels. The catalyst is a production 160 CID oxidation catalyst.

The Engelhard data indicate large differences in sulfuric acid emissions at similarly high exhaust oxygen levels. The reasons for these variations apparently are in the different catalyst formulations. All the formulations were indicated to be proprietary in the Engelhard submission.

The data in Table 7-4 indicate that large sulfuric acid reductions can be achieved by appropriate oxygen level control. The HC and CO penalties shown for the monolithic oxidation catalyst must be carefully minimized in future work.

Exhaust gas temperature

Equilibrium calculations indicate that sulfuric acid emissions can be reduced if the exhaust gas temperature and catalyst operating temperature can be increased. In practice this can be done with exhaust port liners, exhaust pipe insulation, AIR optimization, and catalyst relocation nearer the engine exhaust ports. Exxon has done limited vehicle testing. Their results were shown in Figures 7-2 through 7-5. The temperature increases were about 200°F for the pellets, and the temperature reductions were about 180°F for the monoliths. These data are not absolutely conclusive, but they do suggest that operating temperature increases may provide only marginal improvements in sulfuric acid emissions. Further reductions may be possible at very high operating temperatures, but catalyst durability and exhaust system temperatures are potential problem areas.

7.2 New Sulfuric Acid Control Systems

7.2.1 Air Injection (AIR) Changes

Current AIR systems in normal operation provide large quantities of excess air to oxidation catalysts to assist in the oxidation of HC and CO. These current systems contain valves to divert the compressed air to the atmosphere during: a) decelerating conditions to prevent audible combustion in the exhaust system and b) high engine speed and load conditions to prevent catalyst overtemperature occurances or c) as an alternative to b) conditions when the converter reaches a maximum allowable temperature (generally high speed and load conditions again). The large quantities of excess air of course contain large amounts of oxygen. This has been shown to be undesirable because of the excess oxygen role in the generation of sulfuric acid emissions.

Exxon used a diverter valve in their "limited AIR" vehicles discussed in section 7.1.2. This system represents a simple "on-off" AIR control system. Should simple systems such as this fail to provide statutory HC and CO control, future AIR control systems could become much more sophisticated. Hardware such as electronically controlled clutches (similar to those used for air conditioning compressors) or variable ratio belt drives may be used for improved AIR control. One manufacturer has suggested the use of feedback (oxygen sensor controlled) AIR systems as an alternate to feedback fuel metering. This may be possible, but the fuel metering system would probably need to operate over an A/F ratio band which is narrower than that of current carburetors. With this initial "crude" A/F ratio control the feedback AIR system could possibly eliminate the lean transients which result in high sulfuric acid emissions.

Volvo has reported work on a feedback AIR system. They did not report any test results, but they indicated that HC and CO control was unacceptable. Volvo vehicles now have mechanical fuel injection and it may be more attractive to them to use feedback controlled fuel (not air) metering than to a manufacturer who has not already accepted the cost of fuel injection.

7.2.2 Fuel Metering Improvements

For sulfuric acid emission control at gaseous emission levels more stringent than 0.9 HC, 9.0 CO, 2.0 NOx, the conventional carburetor systems become less attractive from many reasons. These include: 1) a relatively wide A/F operational band, 2) relatively poor fuel distribution, 3) relatively poor emissions repeatability, 4) high transient HC, CO emissions, 5) poor cold start emissions, and 6) poor adaptability to feedback control.

There are many intense efforts going on in the auto industry to find a suitable replacement for the carburetor or to make an improved carburetor. Chrysler is developing a carburetor fuel vaporizer to improve start up characteristics and a fuel injection system. They are evaluating the Dresser sonic carburetor (through Holley) and the Bendix fuel injection system. Ford is evaluating many fuel injection systems including Bosch K-Jetronic, Bosch L-Jetronic, and their own system which uses the vortex shedding principle for air metering. They indicate that the vortex shedding system is too sophisticated and expensive for use in production though it does not appear to be much more sophisticated or expensive than other electronic fuel injection systems. Ford has evaluated the Dresser device and several of their own devices which are similar for some time now. Ford also has reported the development of a system which incorporates fuel injectors into the sonic air metering system. This apparently is to improve the feedback control capabilities of the system. They are also working on feedback controlled carburetors in hopes of making the carburetor compatible with 3-way catalysts. General Motors reported tests using their ITC carburetor, feedback carburetion, and Bendix fuel injection. One Bendix system was reported as "L-Jetronic" which indicates that Bendix is doing work with the Bosch air metering system.

Bendix and Bosch have both offered fuel injection systems which are potentially superior to the carburetor in many respects. The domestic auto industry has not given up the carburetor, however, primarily because of the current carburetor's low cost, the large capital investments in carburetor production facilities, and its ability to achieve current emission levels.

The adoption of 3-way catalyst systems for both sulfuric acid and regulated emissions control would require the use of advanced fuel metering. The capability of using feedback control from an oxygen sensor and the compatibility with other electronic emission control systems suggests that electronic fuel metering of some sort is likely to be adopted in the future.

7.2.3 3-Way Catalyst Systems

Volvo has been the manufacturer with possibly the most extensive test program with 3-way catalysts. It appears that Volvo vehicles with 3-way catalysts may be introduced by 1978. Ford has designated the 3-way plus ox. cat. system as its prime system for 0.41 HC, 3.4 CO, 0.4 NOx. The very low sulfuric acid of feedback controlled 3-way catalyst systems will certainly generate increasing interest by other vehicle manufacturers. The main reason that interest in 3-way catalysts is not even higher is that adequate durability has not been demonstrated at the 0.41 HC, 3.4 CO, levels. Figures 7-7 through 7-12 summarize Volvo durability efforts. The Johnson-Matthey (J-M) catalyst and the Engelhard IIB catalysts are oxidation catalysts, not 3-way catalysts. It must be kept in mind that 3-way catalysts are relatively new, compared to oxidation catalysts. Their current durability performance may be improved in the near future, as more work is done. The recently revised fuel contaminant levels for certification fuels (modified to be consistent with field levels) will help existing and new 3-way catalysts also.

7.2.3.1 3-Way Catalysts Without Feedback

In Table 7-3 Volkswagen has illustrated potential 3-way catalyst emission control systems without feedback. The actual catalysts used by VW were oxidation catalysts (both Pt/Rh), but the calibration techniques

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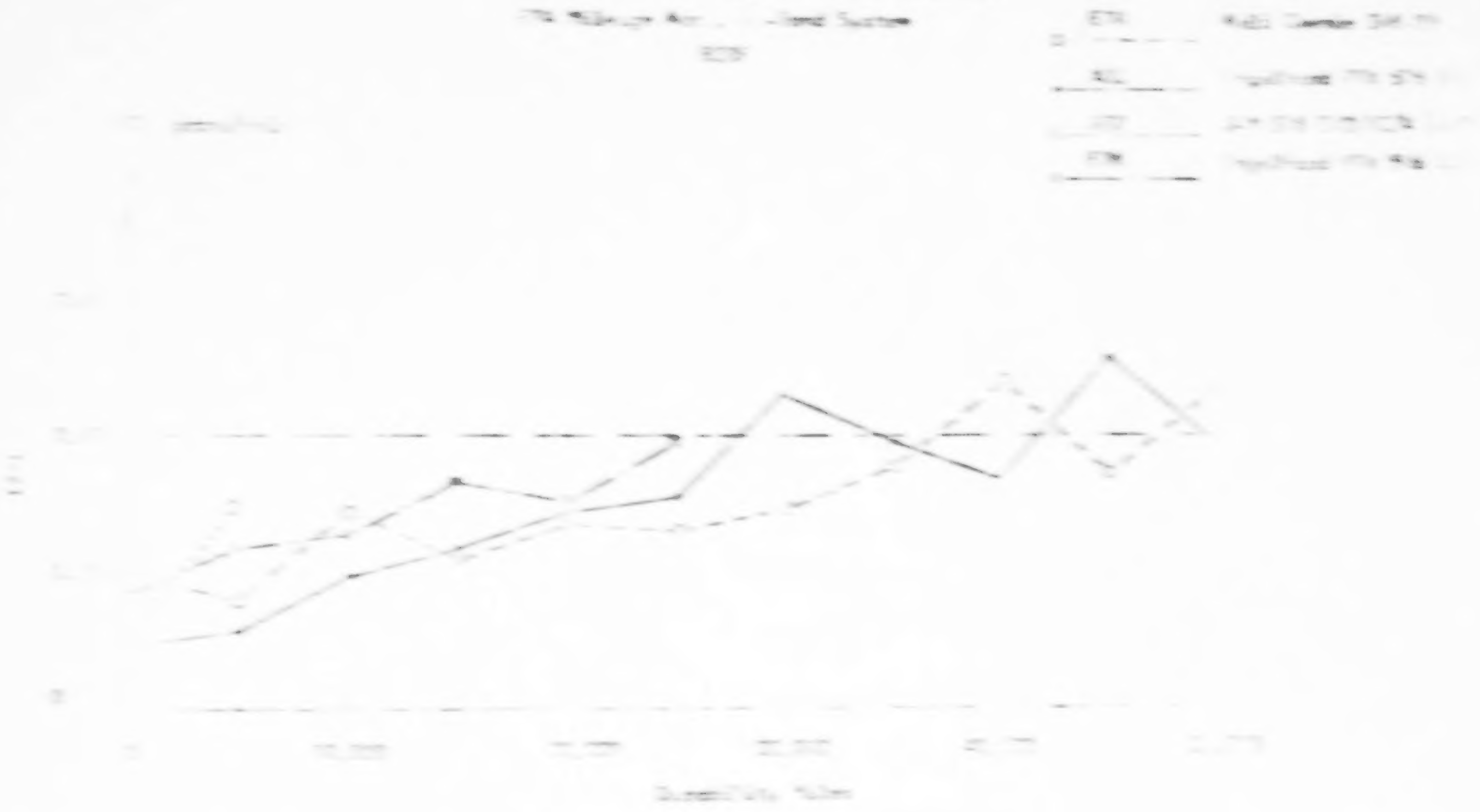

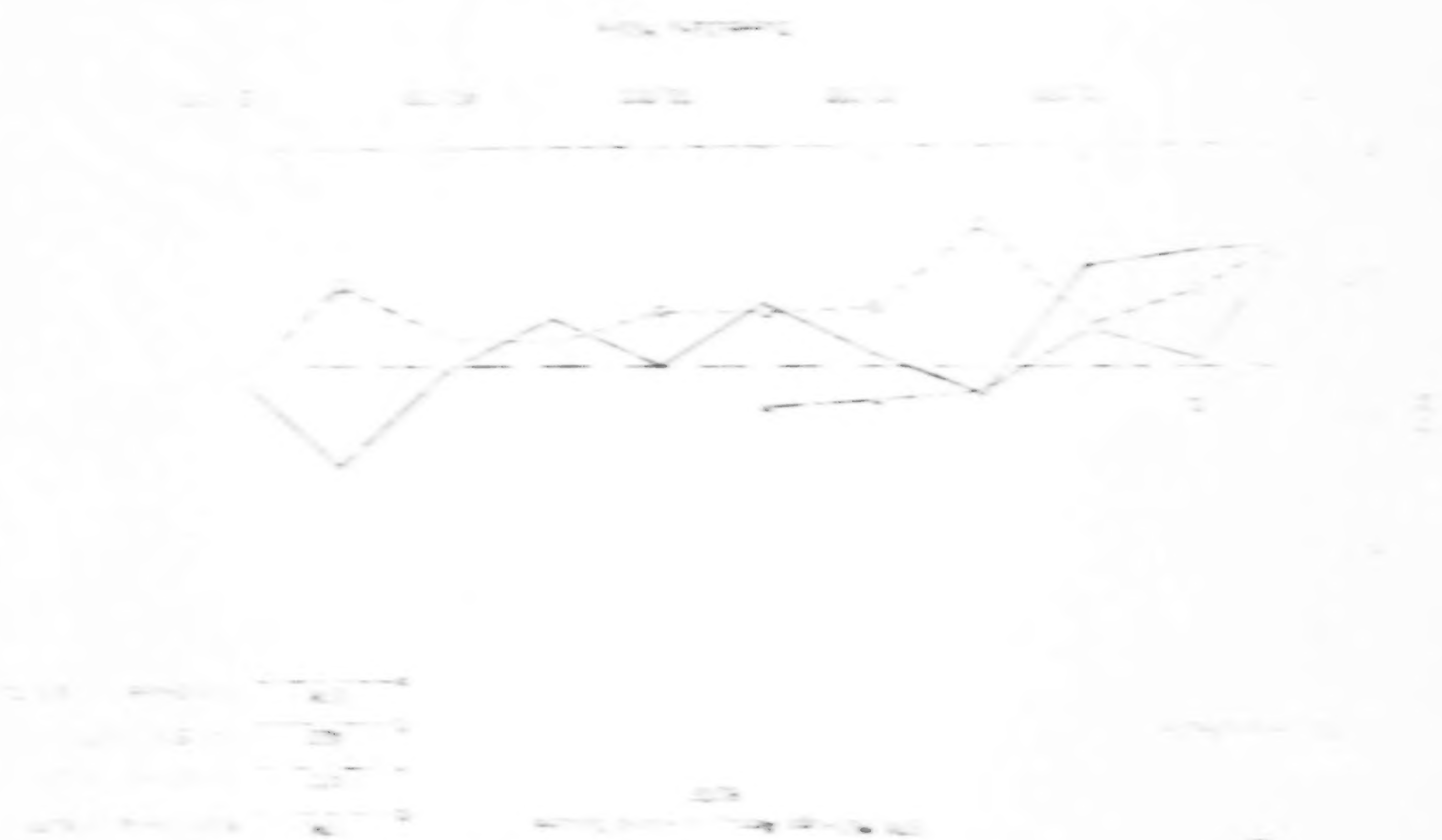

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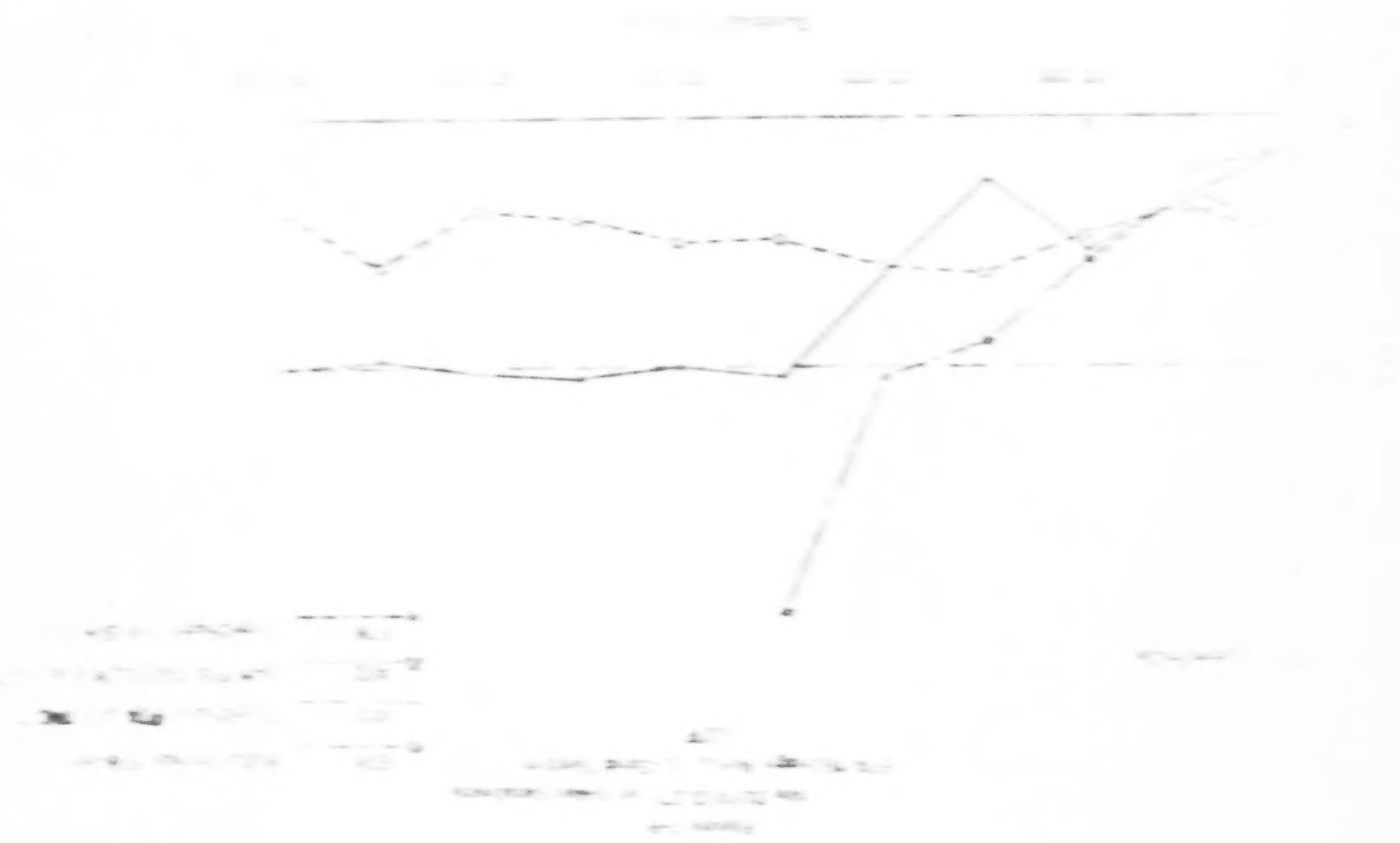

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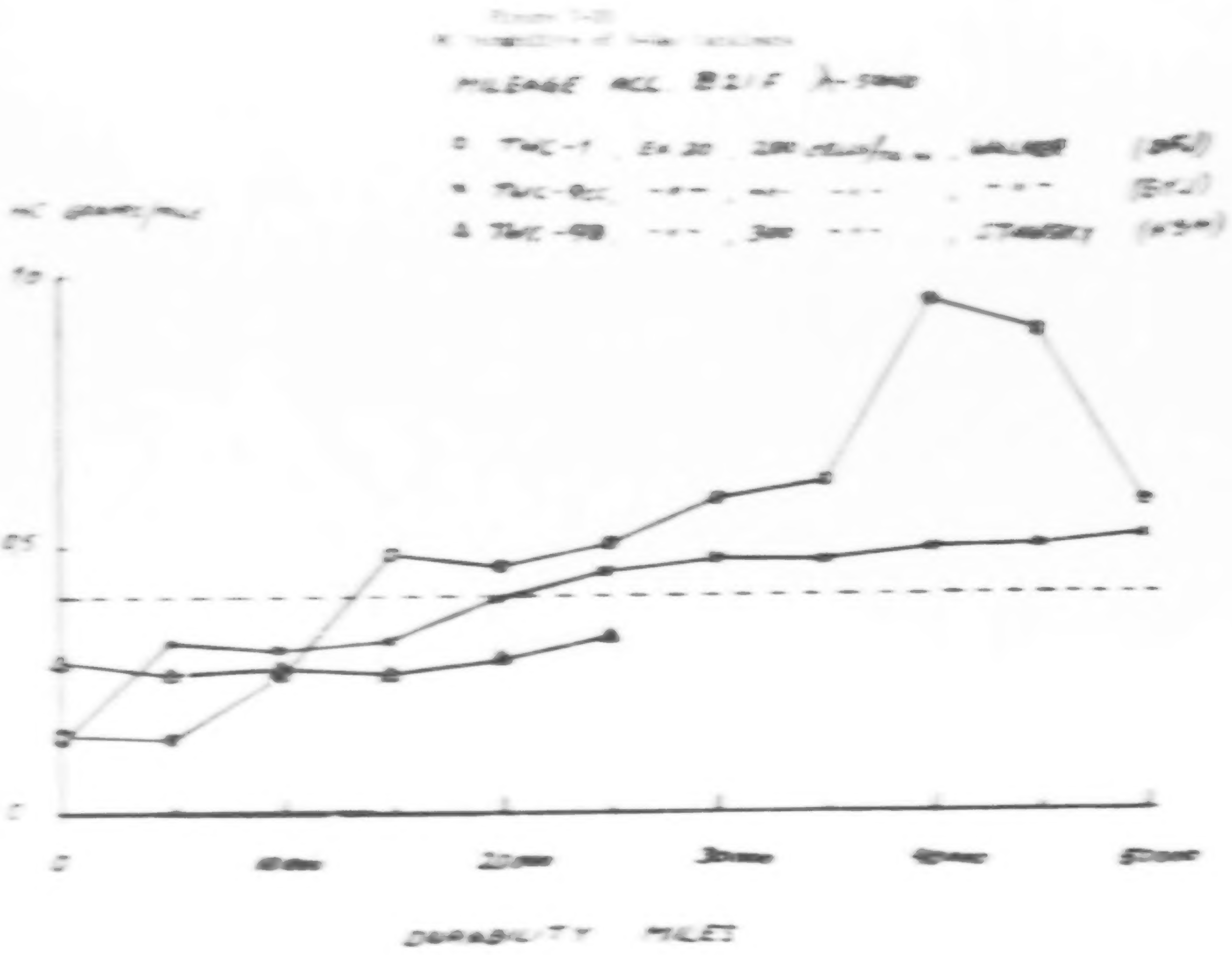
MILEAGE ACC. B21F λ-SOND
○ TWC-1 , Ex 20 , 280 cells/in² , WALKER
● TWC-9CC , — , — , —
△ TWC-4B , — , 300 — , STANDARD
HC grams/mile
1.0
0.5
0
0
10000
20000
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DURABILITY MILES

Figure 7-11

CO Durability of 3-Way Catalysts

MILEAGE ACC. [illegible]

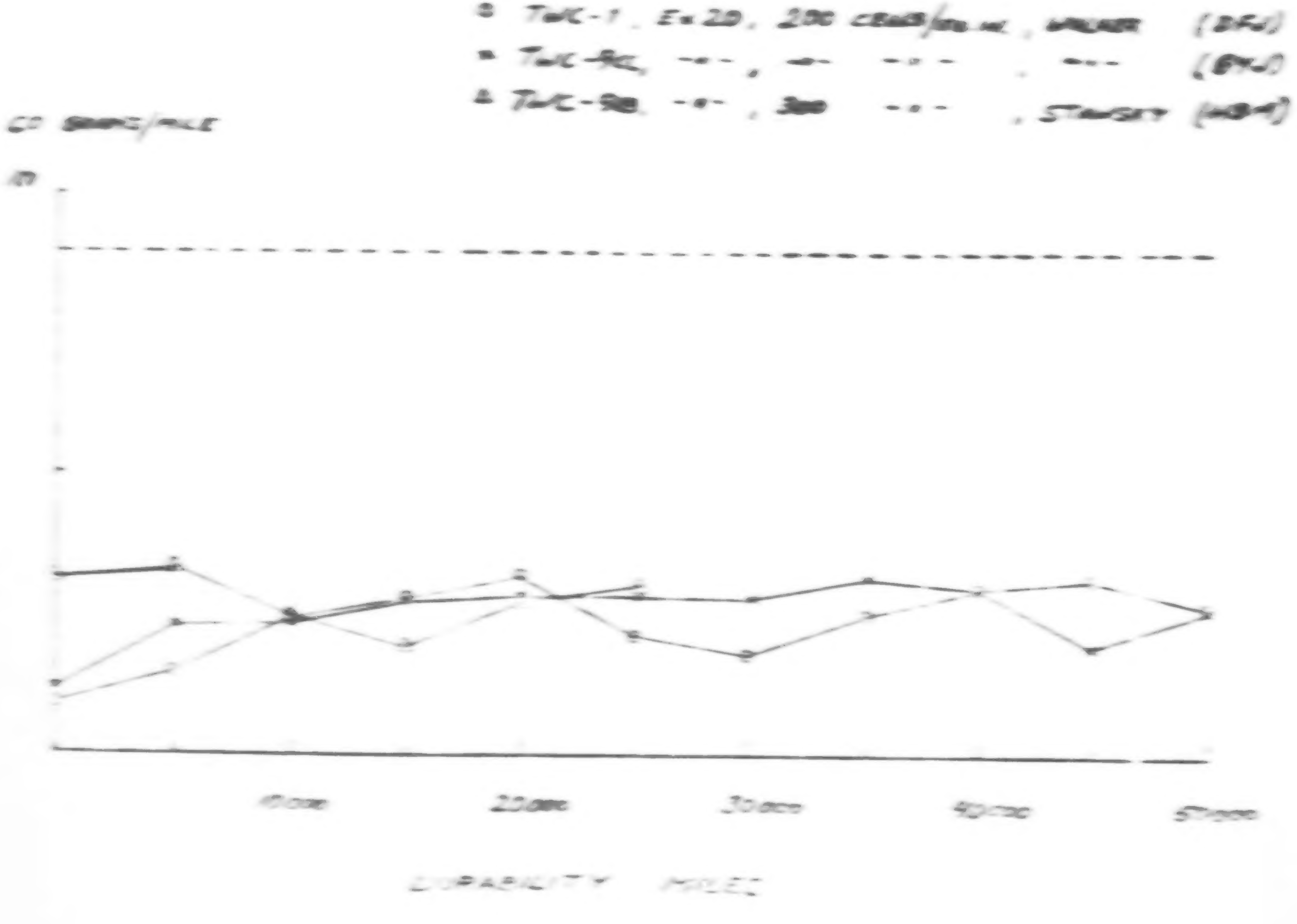
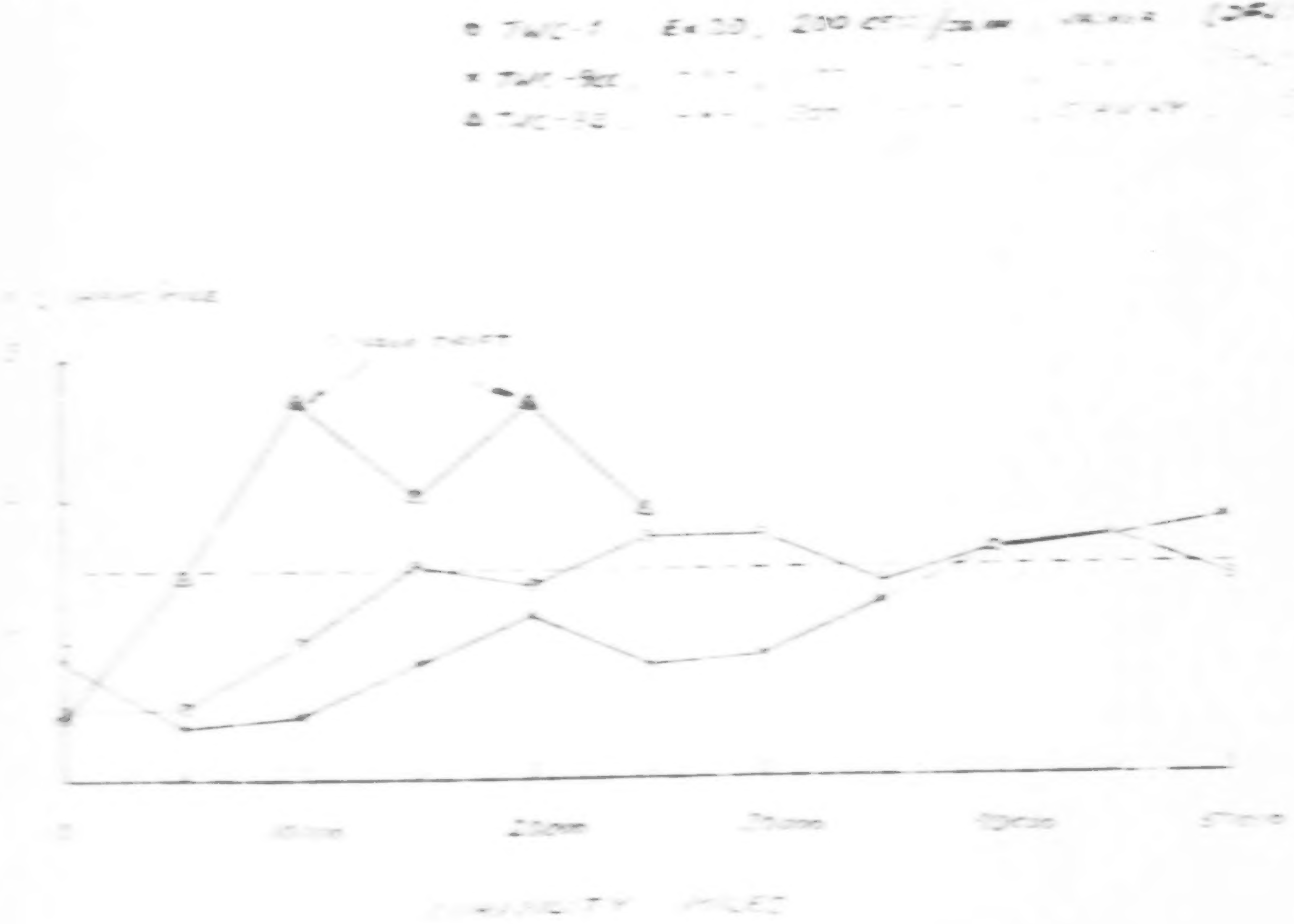


Figure 7-12
The Variability of 3-Way Catalysts
MILEAGE AT [illegible]



are equally valid for 3-way catalyst systems without feedback. The Beetle utilized a lean operating fuel injection system without air injection. The Dasher used rich carburetion and air injection. The low sulfuric acid emissions indicate that the exhaust oxygen levels to the catalyst may have been quite low in both cases. The preferred approach would be the lean fuel injection system because of fuel economy advantages. Other fuel metering systems could be used in place of the fuel injection, but the catalyst efficiencies for HC, CO, and NOx are highly dependent on the capability of the fuel metering system to remain near or within the A/F ratio operating "window". The "window" concept is illustrated in Figure 7-13. HC and CO efficiency are lost during rich A/F ratio fluctuations and NOx efficiency is lost during lean fluctuations.

Table 7-5
Results of Volkswagen Calibration Techniques

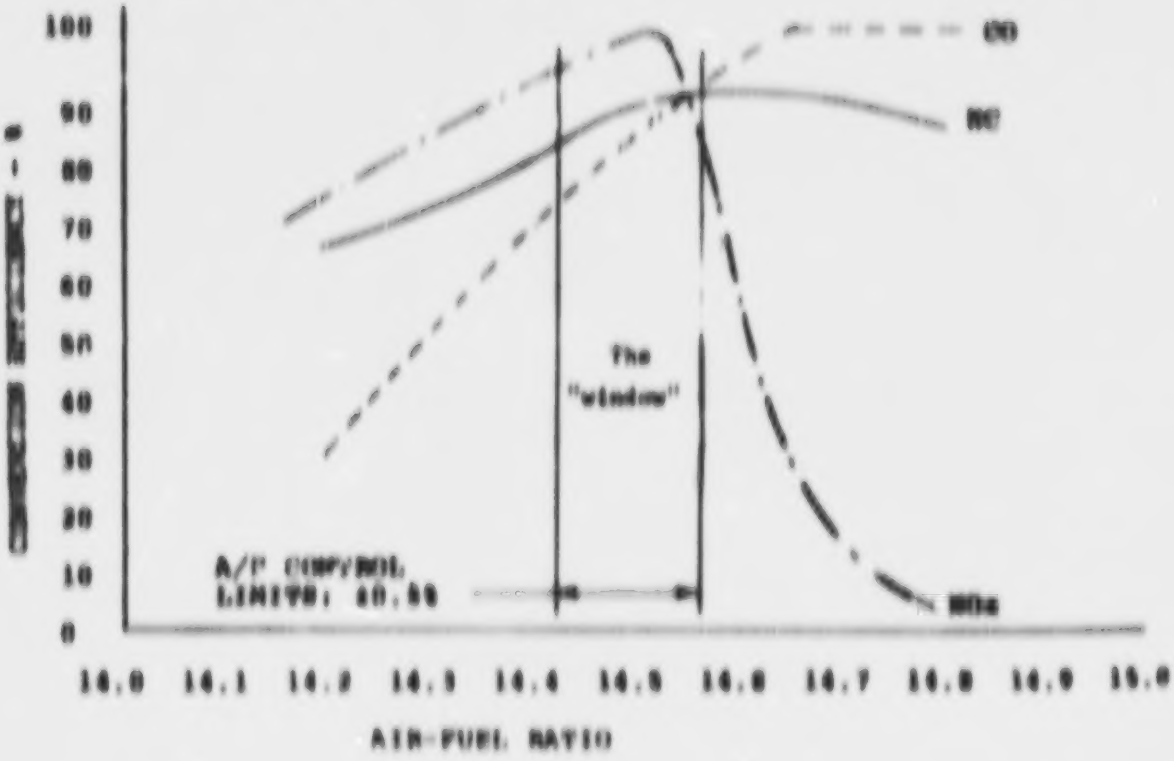
	Test Cycle	HC	CO	NOx	H_2SO_4
		----------	gm/mi	----------	mg/mi
Beetle	75 FTP	.52	5.56	.67	1
Dasher	75 FTP	.55	6.41	1.65	3

7.2.1.2 3-Way Catalysis With Feedback

The use of feedback control to the fuel or air metering system from an oxygen sensor is much more promising than the 3-way catalyst system without feedback, because of its improved capability to operate within the A/F window. A Bosch sensor is shown in Figure 7-14 and a schematic of a current feedback controlled 3-way catalyst is shown in Figure 7-15. This system utilized feedback control of the fuel injection system. The sensor life has been estimated to be greater than 15,000 miles by Bosch. GM indicates a much longer sensor life - possibly 50,000 miles. The sensor cost is estimated to be about five dollars.

Figure 7-11

THREE-WAY CATALYST EFFICIENCY



The Volvo durability data indicate potential down to about 0.41 HC, 3.4 CO, 1.0 NOx without the use of EGR if a catalyst change is considered (see Kali Chemie data). The capabilities of 3-way catalyst systems at 0.4 NOx are uncertain since little has been done with the best EGR systems, but the sulfuric acid emissions would still be expected to be very low (less than 5 mgpm). Table 7-6 presents data from closed loop 3-way catalyst vehicles. All use closed loop fuel injection operated at stoichiometry except for one as noted.

Other fuel metering systems such as carburetors may also be used. Those systems which incorporate electronic fuel control appear most promising due to better time response. The Ford sonic system with electronic injectors is a notable example. Not only does this Ford system appear favorable in terms of cost, but also in terms of potential HC, CO control, potential sulfuric acid control, adaptability to altitude compensation, and adaptability of other electronic emission control devices.

7.2.1.3 3-Way Catalyst Modifications

There has been no incentive to modify 3-way catalysts for lower sulfuric acid emissions as they are already very low, usually less than 5 mgpm when used with the appropriate closed loop hardware. Current emphasis is on improving catalyst durability and widening the A/F ratio "window" of operation.

Though not a catalyst modification as such, Engelhard has indicated (see Figure 7-6) that it is important for HC, CO control at low oxygen input levels to retain palladium in 3-way catalyst formulations. The conversion efficiencies in Figure 7-6 were not confirmed by 1975 FTP results, but indicate improvements in warmed-up efficiency as opposed to improved light off characteristics. Conspicuously absent was an analysis

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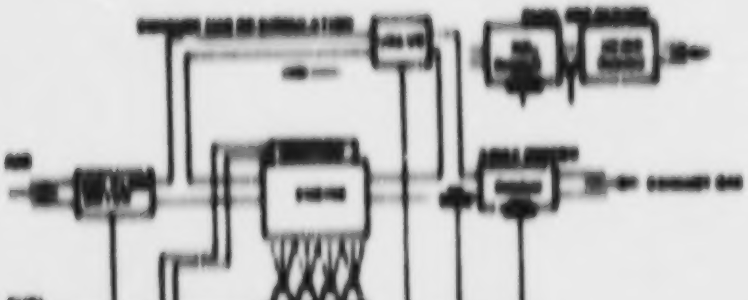
Figure 7-14
Oxygen Sensor

Figure 7-15


EXHAUST GAS RECIRCULATION
AIR
ENGINE
FUEL
THROTTLE POSITION
STARTER SWITCH
INDICATOR LIGHT

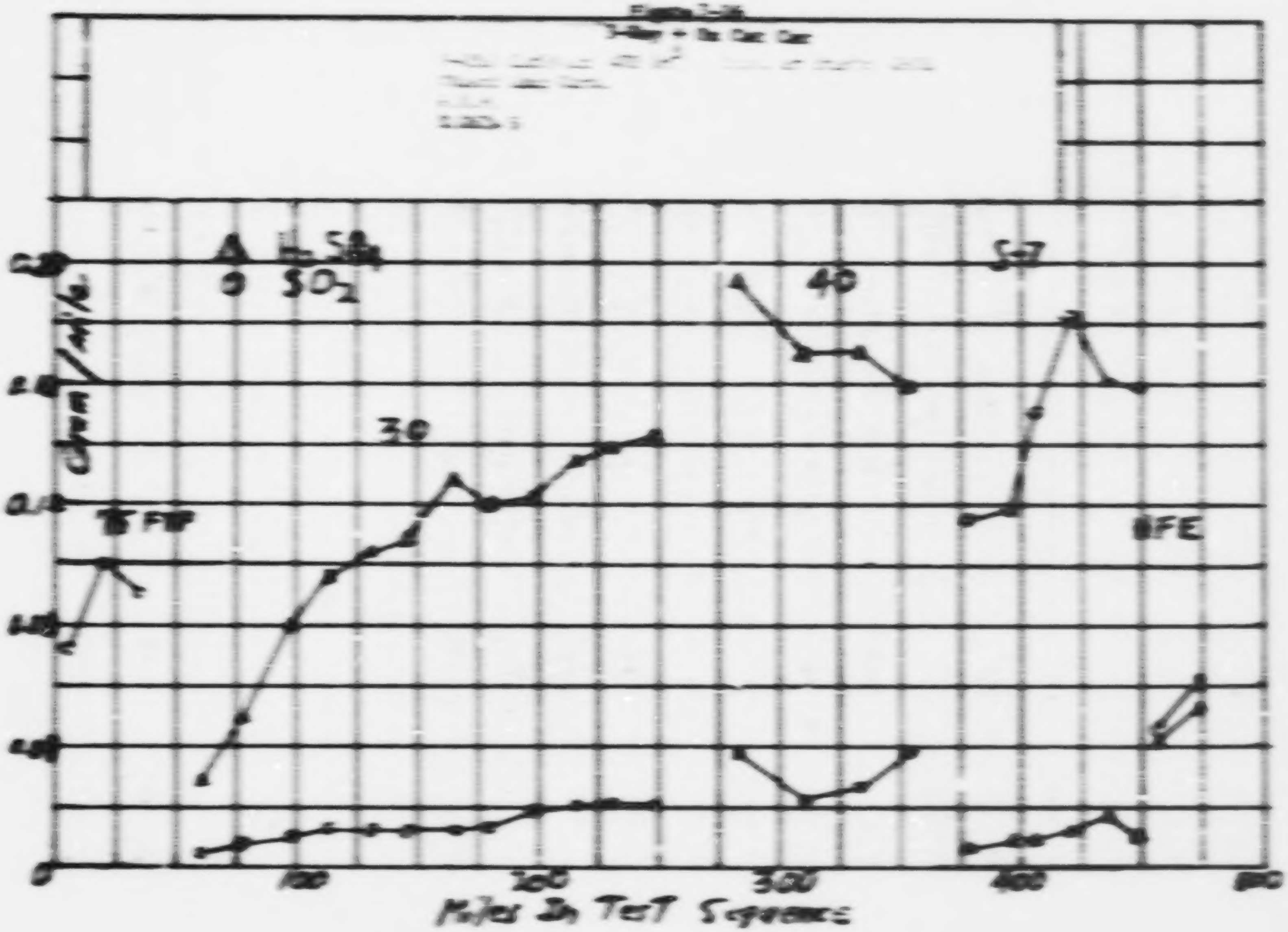
Schematic layout of a closed loop exhaust emission control system of the effects of rhodium, as most 3-way catalysts currently use rhodium with platinum. Engelhard has also indicated that the EPA amendment to the durability fuel specifications which eliminated the minimum lead and phosphorus levels will have "a significant beneficial effect" for 3-way catalyst systems. NOx emissions (apparently NOx durability) are expected to be significantly improved with HC, CO emissions slightly improved.

The perovskite 3-way catalysts developed by DuPont seem to have HC efficiency problems similar to their oxidation catalyst counterparts, but more work is needed in this area.

7.2.4 3-Way Plus Oxidation Catalyst Systems

This system is similar to the 3-way catalyst system with an oxidation catalyst added for clean up of HC and CO. An AIR system would probably be added to insure an oxidizing atmosphere in the second catalyst. Ford has designated this system as its prime system at statutory emission levels, (0.41 HC, 3.4 CO, 0.4 NOx). The sulfuric acid emissions of such a system would depend on the amount of air injected to the oxidation catalyst. If the amount of air were similar to current systems, the sulfuric acid emissions would probably be high. It may be that this amount of air could be much less as the HC and CO conversion requirements should be less than required of current oxidation catalysts. Feedback AIR system control for the oxidation catalyst is feasible and perhaps not too costly, as considerable electronics will already be present to provide stoichiometric mixtures to the 3-way catalyst.

General Motors presented the vehicle data in Figure 7-18 on a 3-way plus ox. cat. system. The vehicle used closed loop carburetion and operated with .067 wt% sulfur in the fuel. This is more than twice the national average sulfur level that all other data in this report has been corrected to (.030). The sulfuric acid emissions of this vehicle


▲ H_2SO_4
● SO_2
Gram/Mile
15 FTP
30
40
S-7
HFE
0
100
200
300
400
500
Miles In Test Sequence

are low over both the FTP and the SC-7. The large differences between sulfuric acid emissions over the 30 SS and 60 SS vs. the FTP and SC-7 cannot be explained without further knowledge of the emission control system and test sequence.

7.2.5 Dual Catalyst Systems

A dual catalyst system contains a reduction catalyst followed by an oxidation catalyst. These systems currently have demonstrated the best durability to date of all potential systems at 0.41 HC, 3.4 CO, 0.4 NOx. Most durability has been run with only marginally acceptable fuel metering systems - conventional carburetors. The use of advanced fuel metering systems should further improve their durability performance.

Table 7-7 contains the sulfuric acid emissions reported on the Chrysler and AMC Gould catalyst equipped cars. The sulfuric acid emissions of the Chrysler car are relatively low. There may be several reasons for this. First is the possibility of low air injection rates as Chrysler reported air pump failure shortly afterward. The proximity of the HC, CO emissions to the statutory levels indicate considerable HC, CO conversion, however. Second is the possibility that the HC, CO oxidation reactions are preferred to the SO_2 oxidation reactions as indicated in Ford lab studies. The CO levels to the oxidation catalyst are high with dual catalyst systems because of their rich A/F ratio calibrations. The sulfuric acid emissions of the AMC car are similar to those of an oxidation catalyst car with air.

7.2.5.1 Reduction Catalyst Modifications

Vehicle manufacturers have expended no efforts to improve reduction catalysts for the purpose of sulfuric acid control. This is because of the priority given to understanding sulfuric acid emissions

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from oxidation catalysts and the apparent dependence of sulfuric acid emissions from a dual catalyst system on the exhaust oxygen level to the oxidation catalyst.

DuPont has also developed perovskite reduction catalysts. Chrysler lab tests indicate that they are very active, but their effect on sulfuric acid emissions is unknown.

Gould has been modifying their reduction catalyst though not for the purpose of decreasing sulfuric acid emissions. The modification is being made to improve the sulfur tolerance of their base metal catalyst. This problem has not been reported for other reduction catalysts.

7.2.6 Start Catalyst Systems

A start catalyst is a low thermal inertia oxidation catalyst which is mounted near the exhaust ports of the engine. The light-off time is more important, and resistance to "breakthrough" is less important than for a main catalyst. Both GM and Chrysler considered the use of start catalysts before suspension of the 1977 emission standards.

Start catalysts may be useful for sulfuric acid emissions and gaseous emissions control for vehicles with and without main oxidation catalysts. A warm up AIR system would probably be needed in either case. Without a main catalyst, the start catalyst would assist in lowering emissions to achieve the .9 HC, 9 CO, 2.0 NOx levels. It appears that current start catalyst durability may not be sufficient for continuous operation, so a start catalyst must be removed from the exhaust stream after the main catalyst has lit off or after cold start enrichment has ended if a main catalyst is not used. If the DuPont catalyst is shown to have the high temperature capability claimed for it, it might make a natural start catalyst, especially if it could be left on-stream all the time. The resulting system could be cheaper than a switched-out start catalyst.

Chrysler reported [illegible] results from a 360 CID Cordoba with a start catalyst, a main catalyst, and AIR. The sulfuric acid emissions ranged from 16 to 27 mgpm with .008% sulfur in the fuel.

For the no main catalyst case, sulfuric acid emissions would increase slightly over non-catalyst vehicles, but would be less than for vehicles with main catalysts and high exhaust O_2 levels. With a main catalyst, the start catalyst could offer improved cold start HC, CO control so that exhaust O_2 levels and sulfuric acid emissions could be reduced.

Start catalysts could be used in 3-way catalyst systems which use feedback AIR control in place of feedback fuel metering. The sulfuric acid penalty would be very small, and the improved light off characteristics would assist in HC, CO, and NOx control. Start catalysts could similarly be used in 3-way plus ox. cat systems. Current 3-way systems do not use the AIR system and would have to add it to gain start catalyst benefits.

7.2.7 Super Early Fuel Evaporation (Super EFE)

Super EFE systems are quick heat intake manifolds developed by General Motors. These systems are used for start up. They block the exhaust flow from both banks of a V-8 engine and divert the exhaust flow under the floor of the intake manifold and out a third exhaust pipe as in Figure 7-17. The floor of the intake manifold is a high heat transfer, finned plate. GM has stated that problems with super EFE include: 1) coking of the heat transfer plate, 2) casting difficulties, 3) durability, and 4) cost and complexity. However, resolution of these problems

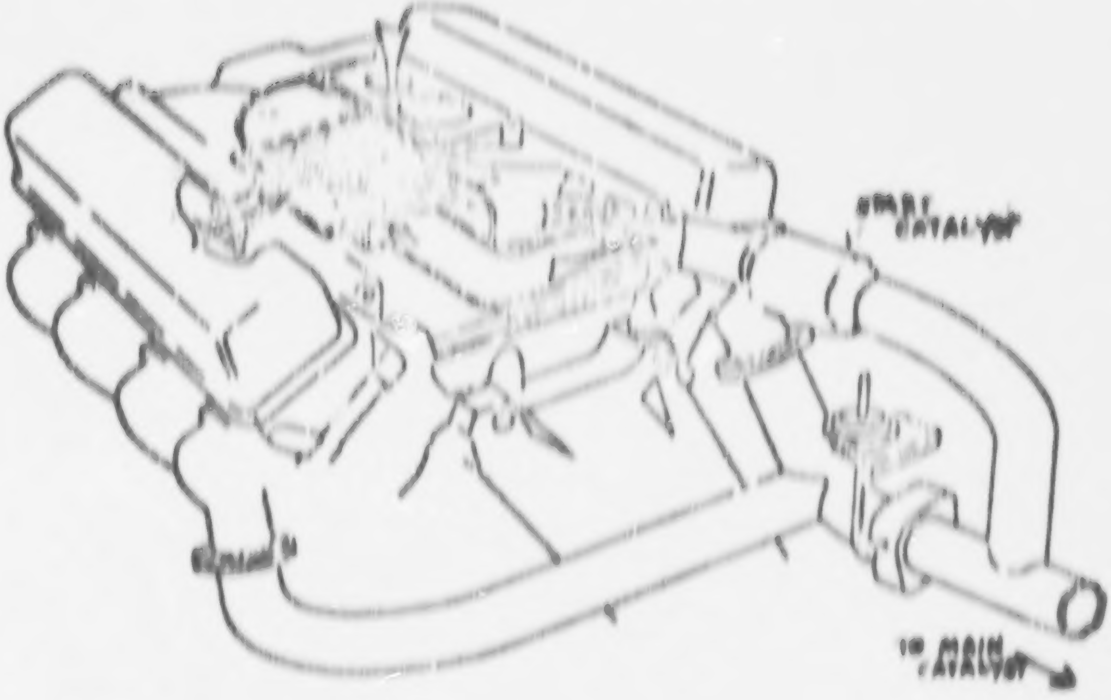
START CATALYST
TO MAIN CATALYST

FIGURE 7-17

Super EFE with Start Catalyst

may be possible and such systems may be found perferable to exhaust oxygen level control systems at low HC, CO, and NOx levels.

The super EFE system with a conventional carburetor has been reported to have achieved the 0.41 HC, 3.4 CO, 2.0 NOx levels without catalytic treatment of the exhaust. Thus the sulfuric acid emissions would be very low. A big fuel economy penalty was reported, but a start catalyst in the third exhaust pipe as in Figure 7-17 could assist in gaining HC and CO control that could be traded off for more optimal fuel economy. The addition of a main catalyst could further improve the HC, CO control and/or fuel economy.

7.2.8 Electronic Emission Control Systems

Both Ford and Chrysler have plans for the introduction of electronic spark control on some 1976 model year vehicles. Electronic fuel injection is in production on two GM vehicles. Ford and Chrysler are developing electronic EGR control systems. All three are developing electronic fuel metering systems. Evidence is accumulating that electronic emission control systems will be used in conjunction with catalysts to achieve statutory emission levels. Sulfuric acid emission control will provide another reason for going to feedback controlled electronic fuel metering systems or air injection systems. Once the cost of either of these systems is accepted, full electronic control of many functions may soon follow. These could include:

- engine air/fuel metering
- exhaust air injection control
- spark control
- EGR control
- altitude compensation
- transmission shift points
- anti-skid control of the vehicle

7.8.9 Sulfuric Acid Traps

7.8.9.1 Mechanical Traps

Sulfuric acid traps involve removing sulfuric acid after it is formed in the catalyst by either mechanical or chemical means. Mechanical traps would be similar to traps developed by DuPont and Ethyl for lead additives. These traps work by centrifugally removing exhaust particulates. While these traps have been demonstrated adequately for lead compounds, there is serious questions that they would work for sulfuric acid. Sulfuric acid would probably not condense as a particulate in the exhaust system but still be in gaseous form. Mechanical traps are ineffective in removing gases. Chemical traps which remove sulfuric acid by an acid-base chemical reaction seem to be the only feasible type of trap.

7.8.9.2 Chemical Traps

Much of the work on chemical traps has been done by EPA through contract with Exxon Research and Engineering. Both GM and Ford have started trap programs but have extremely limited results to report.

Most of the work that has been done involves screening various materials for use in the trap. The screening is done in a laboratory apparatus that uses a synthetic exhaust gas blended from gas cylinders to contain sulfuric acid, SO_2, and other components found in automotive exhaust. Screening materials for use in traps involves examining several criteria as listed below:

Reactivity for sulfuric acid
High capacity of material for absorption per unit volume
Small volume increase of material after trapping

Thermal stability of material
No adverse side reactions
Low water solubility
Low toxicity of material
Little attrition of material with mileage

These criteria were developed by Exxon. Many of the materials screened by Exxon are listed in Table 7-8.

Table 7-8
Trap Materials Screened by Exxon

85% CaO, 10% SiO_2, 5% Na_2O
Al_2O_3
BaO
80% CaO, 20% SiO_2
MgO
85% MgO, 10% SiO_2, 5% Na_2O
$CaCO_3$ as marble chips
ZrO_2 (zirconia)
Micro-cel
ZnO
97% CaO, 3% aluminum stearate
MnO_2

These tests show the calcium oxide mixtures to be most effective in reacting with sulfuric acid. The calcium carbonate also seemed promising. The mixture of calcium, silicon, and sodium oxides removed well over 90% of the sulfuric acid.

GM has also screened a number of compounds including both active materials on alumina supports and bulk materials with no support. The on a catalyst vehicle. The vehicle ran for 15,000 miles and the trap was still removing about 95% of the sulfuric acid emitted from the catalyst. The pellets in the trap showed almost no attrition products and had excellent physical stability. However, pressure drop across the trap increased from an initial value of 1,000 pascals to a final value of 30,000 pascals. The trap material expanded considerably as sulfate was absorbed thus filling in void volume and causing the much higher pressure drop. The pressure drop was great enough so that the vehicle would hardly operate. Additional work is necessary in designing a trap that is effective and yet does not have these pressure drop characteristics.

GM is working on a trap that increases in volume as the trap material expands. The trap contains a moveable plate held in place by a spring which moves as the trap material increases in volume. This trap has not been tested yet.

Exxon also tested a trap containing calcium carbonate in the form of marble chips. The vehicle test showed low reactivity for sulfuric acid indicating calcium carbonate, at least in this physical form, is not a good trap material.

Exxon is also examining use of trap material of a ring type geometry versus the pellets originally used. The rings have sufficient void volume that a satisfactory pressure drop should be obtained. Exxon is fabricating rings made of a suitable trap material and will test them on a vehicle shortly.

Exxon is also examining other sorbent materials which expand less than the CaO-Na_2O. It seems the presence of the Na_2O results in both SO_2 and SO_3 absorption. A less reactive material resulting in SO_3 absorption but no SO_2 absorption should have less expansion. Exxon is screening apparatus used by GM involves passing actual engine exhaust through 10 trap samples simultaneously. While this apparatus enables screening of many materials, it does not allow the efficiency of the materials, to be determined accurately since there is no way to measure absorption for each of the individual materials. Also, it is not known that uniform flow was obtained for all 10 samples. GM has tested the following general types of materials:

Supported materials
  noble metals on alumina-5 samples
  metal oxides on alumina-17 samples
  alkali-alkaline earth oxides on
  alumina - 5 samples
  miscellaneous - 17 samples

Bulk materials
  oxides-hydroxides - 8 samples
  mixed oxides-hydroxides - 5 samples
  metallic systems - 7 samples
  miscellaneous - 2 samples

GM found most of the supported materials to have satisfactory physical durability but generally low reactivity towards SO_3 since less than 60% of the SO_3 was absorbed. Many of the bulk materials had poor physical durability since they broke apart and fragmented. GM feels that a calcium oxide material seems to offer the most potential at this time. This is in agreement with the Exxon findings.

Even more limited vehicle tests have been done using traps. Most of the vehicle test work has been done through an EPA contract with Exxon. Exxon tested the $CaO-SiO_2-Na_2O$ formulation in a trap installed screening a variety of mixtures of calcium oxide with other compounds. Unfortunately, these other compounds are not as effective as the CaO-SiO_2-Na_2O for sulfuric acid but seem to have adequate reactivity. The most promising mixtures to date contain either diatomite or Portland cement in addition to the calcium oxide. The most promising materials from this extended screening project will be vehicle tested. The vehicle testing will be complete early in 1976.

The work done to date on sulfuric acid traps is very promising in that it shows it is possible to build a vehicle trap that removes sulfuric acid. However, a number of problems must be resolved before these traps are ready for vehicle application. It is not known at this time whether sulfuric acid traps can be an option to meet a sulfuric acid standard in 1979.

SECTION 8

WHAT ABOUT SULFURIC ACID EMISSIONS FROM OTHER ENGINES?

8.1 "Lean Burn" Engine

The term "lean burn" engines refers to conventional Otto cycle engines which have air-fuel metering calibrations leaner than a stoichiometric air-fuel ratio. The stratified charge engines which also operate leaner than stoichiometric will be considered in Section 8.2.

8.1.1 Non-Catalyst Vehicles with Lean Burn Engines

Non-catalyst vehicles using lean burn engines and lean thermal reactors have emissions potential down to at least 0.9 HC, 9 CO, 2.0 NOx. As seen in Table 8-1, sulfuric acid emissions from these vehicles are very low and about equal to other non-catalyst vehicles. These systems would compete with non-AIR, catalyst systems for use in production at the 0.9 HC, 9.0 CO, 2.0 NOx levels. The non-catalyst, lean burn cars would be expected to have small fuel economy losses and somewhat lower sulfuric acid levels when compared to non-AIR, catalyst vehicles at these emission levels.

8.1.2 Catalyst Vehicles with Lean Burn Engines

Lean burn plus oxidation catalyst vehicles (without AIR or start catalysts) are potentially competive at the .9 HC, 9 CO, 2.0 NOx levels. Table 8-2 illustrates that sulfuric acid emissions of catalyst vehicles with lean burn engines are somewhat lower than catalyst vehicles equipped with an air pump, but higher than current production non-AIR vehicles. These levels are assumed to be attributable to the excess oxygen in the exhaust.

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8.2 Stratified Charge Engines

Stratified charge (SC) engines have been investigated by EPA and the automotive industry both for low emissions levels and improved fuel economy. SC engines have been produced with direct cylinder injection, (PROCO and the Texaco TCCS) and with divided, separately fueled combustion chambers, (Honda CVCC). Additionally, the direct injection SC engines have been tested with catalytic converters.

SC engine vehicles have excellent emission potential coupled with potential for improvements in fuel economy over the conventional Otto cycle engine. Since SC engines are lean burning engines, it would be expected that those SC engines which also incorporated a catalyst to achieve 0.41 HC, 3.4 CO would have high sulfuric acid emissions. The tests reported to date in Table 8-3 seem to indicate that the two systems tested have sulfuric acid emission levels more equivalent to non-AIR catalyst equipped vehicles. The reasons for this are not known presently, but may be related to exhaust temperature. Those engines which have no catalysts are comparable to vehicles with conventional engines without catalysts.

8.3 Diesel Engines

Few sulfuric acid emission data have been accumulated using the Diesel engine in LD vehicles. The data are presented in Table 8-4. These data indicate the Diesel cars had sulfuric acid emission levels like those of vehicles equipped with catalysts, being approximately in between the catalyst no-AIR and the catalyst with AIR results, and closer to the lower of the two levels.

It should be pointed out however, that the fuel sulfur level was seven times higher than the previously reported gasoline levels of

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0.03%. Diesel fuel has about 0.2% as the average national fuel sulfur level. If a desulfurized Diesel fuel were utilized, it is conceivable that the Diesel engine would achieve sulfuric acid levels of the non-catalyst gasoline vehicles.

A word of caution concerning these data should be noted. Concern has been shown by a number of test facilities and investigators that the amount of particulate carbon emitted by the Diesel engine may be masking the true sulfate levels observed during the sulfate test procedure. Further work must be conducted to resolve this controversy.

8.4 Other Lean Engines

A Williams gas turbine was run at the Dow-Midland facility during 1973 and the sulfate results reported were .05 mgpm on the 1975 FTP and .4 mgpm during a 50SS. No preconditioning was reported. There was difficulty with the vehicle test set-up and the sulfate results may not be representative of the true results obtainable.

SECTION 9

WHAT IMPACTS ARE LIKELY TO ACCOMPANY SULFURIC ACID CONTROL?

Since there has not been a significant amount of work done specifically for sulfuric acid control, this section will discuss future gaseous emission levels, the emission control options open to manufacturers to achieve those gaseous emission levels, the estimated sulfuric acid emissions of each control option, and the other impacts as related to each control option. These other impacts will include cost and fuel economy. A general discussion of lead time and unregulated pollutants will be presented with special attention given to the lead time requirements for critical hardware. The relevant time frame for this section is 1979-1980.

9.1 Cost, Fuel Economy, and Sulfuric Acid Emissions of Potential Emission Control Systems

The following tables indicate the emission control systems which are options to the manufacturers for 1979-1980. These system selections are appropriate for automobiles up to 4000 pounds inertia weight. Systems for heavier vehicles may be somewhat different, but certainly the vast majority of 1979-1980 vehicles would be included in this analysis. Only the Otto cycle engine was considered in this analysis as it will still be the predominant powerplant in 1979-1980. Stratified charge and Diesel engines will probably increase their market shares, but will still represent only small portions of the total sales.

The systems abbreviations used in the following tables are:

PEGR = Proportional exhaust gas recirculation
AIR = air injection system
IAIR = improved air injection system (includes proportional AIR
and accel air control)
LB = lean burn engine
OC = oxidation catalyst
SC = start catalyst
3W = 3-way catalyst
DC = dual catalysts (reduction plus oxidation catalysts)
SEFE = super early fuel evaporation system (i.e. 8 cylinder EFE)
IFM = improved fuel metering (i.e. Dresser carburetor or its
equivalent)
CLFI = closed loop fuel injection
TR = thermal reactor
RTR = rich thermal reactor
RCR = reactor-catalyst-reactor (i.e. Questor system)

The cost estimates included Table 9-1 through 9-7 are complete emission control system or subsystem costs (sticker prices) in 1976 dollars. Total system costs are based on the individual component costs in Table 9-1. None of the system costs include catalyst change costs. It is possible that in certification at emission levels below 0.4 HC, 3.4 CO, 1.0 NOx, any of the catalytic systems could require a catalyst change.

The multiplicative fuel economy factors are based on a 1976 model year fuel economy factor of 1.00. The highest fuel economy factor of 1.08 indicates that an estimated 8% improvement in fuel economy will be accrued by 1979-1980 by systems changes alone. This does not include changes in model mix (the switch to lighter cars), improved transmissions, reduced aerodynamic drag and rolling resistance, or any of the myriad of other changes planned for introduction in that time frame to improve fuel economy.

Table 9-1*
Emission Control Component Costs
(Jan 76 Dollars)

Component	Report Form Estimate of Cost
1. PCV Valve	3
2. Evap Control	15
3. Transmission Controlled Spark (TCS)	5
4. Anti-Dieseling Solenoid	6
5. Intake air heater	[illegible]
6. OSAC spark control	[illegible]
7. Hardened valve seats	[illegible]
8. Air system	[illegible]
9. Advanced Air System	[illegible]
10. [illegible]	[illegible]
11. EGR manifold	[illegible]
12. Electric choke	[illegible]
13. [illegible]	[illegible]
14. Timing & other control modulation valves	[illegible]
15. OX catalyst	[illegible] Pellet [illegible] Big Monolith [illegible] Each
16. NOx catalyst	[illegible]
17. Misc. mods thru '74	[illegible]
18. EFI	[illegible]
19. O_2 Sensor and feedback electronics	[illegible]
20. 3-way catalysts	[illegible]
21. Thermal Reactor	[illegible]
22. Improved Exhaust System	[illegible]
23. [illegible]	[illegible]
24. OX Pellet cat chg.	[illegible]
25. Mono cat chg.	[illegible]
26. EFC	[illegible]
27. Start catalyst	[illegible]
28. Improved fuel metering	[illegible]
29. Super EFC	[illegible]

* from "Tradeoffs Associated with Possible Auto Emission Standards" prepared by the Emission Control Technology Division, Mobile Source Pollution Control, February 1976.

The sulfuric acid emissions of each control option are stated as being less than or equal to a number. This number represents our estimate of a value which could be achieved by the vast majority of vehicles using the specified control system, though not necessarily by all vehicles using that control system.

The use of sulfuric acid traps has not been considered in this section because of uncertainties in their availability for the 1979-1980 model years.

Table 9-2
Systems for 1.5 HC, 15.0 CO, 2.0 NOx for 1979-1980

System	Cost	Fuel Economy Penalty	H_2SO_4 Emissions g/mi
EGR+OC*	[illegible]	[illegible]	[illegible]
EGR+AIR+OC	[illegible]	[illegible]	[illegible]
AIR+OC	[illegible]	[illegible]	[illegible]
LB	[illegible]	[illegible]	[illegible]
LB+EFI	[illegible]	[illegible]	[illegible]
LB+OC	[illegible]	[illegible]	[illegible]

*System most likely to be used, as indicated by manufacturers

Discussion of Table 9-2

Systems

The EGR+OC system is similar to the current Federal control systems of most manufacturers. By 1979-1980 this could actually approach an open loop, 3-way catalyst system. The EGR+AIR+OC system may not be used as it offers no advantages over EGR+OC. The LB+EFI system is very attractive because of its low cost, low sulfuric acid emissions, and good fuel economy. The EFI system is the key to this system as it is necessary to cheaply retain good fuel economy. The EFI system is not ready for production at this time, but it could possibly be ready for use in 1979.

Cost

The cost advantages of LB and LB+EFE have been noted already. The LB+TR system also offers cost advantages with no other penalties at this emission level. Thermal reactor development programs in the industry are ongoing, but at a rather low priority.

Fuel Economy

HC and NOx emissions will not create fuel economy problems except for LB only systems which would have to use some retard for HC, NOx control.

H_2SO_4 Emissions

The sulfuric acid emissions for the AIR+OC system may be unrealistically high if the start catalyst is switched out of the exhaust system. Since no such system has been tested, the 30 mgpm estimate was used and is considered to be quite pessimistic. The high sulfuric acid emissions of the EGR+AIR+OC system indicate that air injection systems which create very high exhaust oxygen levels in oxidation catalyst systems cannot be tolerated if low sulfuric acid emission levels are needed.

Table 9-1
Systems for 0.9 HC, 9.0 CO, 2.0 NOx for 1979-1980

System	Cost	Fuel Economy Factor	H_2SO_4 Emissions, mgpm
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

Systems most likely to be used, as indicated by manufacturers.

Discussion of Table 9-1

Systems

The EGR+OC system may again approach the open loop 3-way catalyst system. The 1976 certification results conclusively indicate that these systems can certify at .9 HC, 9 CO, 2.0 NOx. The AIR systems are now partially developed as proportioning valves and are in production by one small manufacturer. The axel control system is not developed, but could be available by 1979.

The LB+EFR system is again very attractive for initial cost, but fuel economy considerations suggest that port liners and a thermal reactor or other aftertreatment would be required.

Fuel Economy

Fuel economy considerations suggest that a thermal reactor should be added to the LB+EFR systems. EGR+OC systems need EFR at this emission level to avoid retard for NO control.

H_2SO_4 Emissions

The sulfuric acid emissions of the EGR+AIR+OC may be overestimated. Much greater improvements in sulfuric acid control have been achieved via AIR system improvements, but at HC, CO penalties. Until the HC and CO/sulfuric acid emissions/exhaust oxygen level relationships are better understood, the 10 mgpm estimate will be used.

Table 9-4
Systems for 0.41 [illegible], [illegible], [illegible] for 1979-1980

System	Cost	Fuel Economy Factor	[illegible]
[illegible]*	235	0.90	.80
[illegible]	290	0.90	.30
[illegible]*	305	1.00	.70
[illegible]	300	1.00	.60
[illegible]	150	0.70	.10
[illegible]	215	0.85	.20
[illegible]	280	0.95	.80
[illegible]	275	0.95	.30
[illegible]	310	1.00	.70
[illegible]	325	1.00	.60
[illegible]	180	1.00	.30
[illegible]	200	1.00	.30
[illegible]	200	1.00	.10
[illegible]	410	1.00	.80
[illegible]	380	1.00	.30
[illegible]	405	1.00	.30

*Systems most likely to be used, as indicated by manufacturers.

Table [illegible]

Systems for 0.41 HC, [illegible] CO, [illegible] NOx for 1978-1980

System	Cost	Fuel Economy Penalty	[illegible]
[illegible]	[illegible]	0.00	[illegible]
[illegible]	[illegible]	0.05	[illegible]
[illegible]	[illegible]	1.00	[illegible]
[illegible]	[illegible]	1.00	[illegible]
[illegible]	[illegible]	0.00	[illegible]
[illegible]	[illegible]	0.00	[illegible]
[illegible]	[illegible]	1.00	[illegible]
[illegible]	[illegible]	1.00	[illegible]
[illegible]	[illegible]	0.05	[illegible]
[illegible]	[illegible]	1.00	[illegible]
[illegible]	[illegible]	0.05	[illegible]
[illegible]	410	1.00	[illegible]
[illegible]	[illegible]	1.00	[illegible]
[illegible]	[illegible]	1.00	[illegible]
[illegible]	[illegible]	0.00	[illegible]

*Systems most likely to be used as indicated by manufacturers.

**EGR on large cars

Discussion of Table 9-4 and 9-5

Systems

LB+OC+TR+IFM and LB+OC+IFM systems could approach open loop 3-way catalyst systems if desirable. The IFM would be used to control the exhaust oxygen level, and sulfuric acid emissions would be much reduced in that case. The [illegible] systems are just appearing, even though they may be viable at higher emission levels. They were brought in here because this is the only emission level they have been tested at.

Cost

The most attractive systems are clustered at about $300 initial cost, and SC+CLFI has become competitive in price for the first time.

Fuel Economy

The EGR+IAIR+OC systems and the SC+CLFI systems are no longer achieving optimal fuel economy as they become NO control limited. The [illegible] systems are not competitive in fuel economy until they evolve to [illegible].

H_2SO_4 Emissions

The sulfuric acid emissions of the IAIR systems become very critical in terms of leaving a large number of control system options open to the vehicle manufacturers. The 15 mgpm level of sulfuric acid emissions leaves many technical options open at 1.5 HC, 15 CO, and 2.0 NOx and at 0.9 HC, 9 CO, 2.0 NOx, but very few are left at 0.41 HC, 3.4 CO, and 2.0 NOx. The sulfuric acid emission level now needs to be 30 mgpm to leave many of the technical options open.

Table 9-6

Systems for 0.41 HC, 3.4 CO, 1.0 NOx for 1979-1980

System	Cost	Fuel Economy Factor	H_2SO_4 Emissions mg/mi
EGR+AIR+OC+EI	285	0.95	≤70
EGR+PAIR+OC+EI	300	0.95	≤40
EGR+AIR+QSFD+OC+EI	310	1.00	≤70
EGR+PAIR+QSFD+OC+EI	325	1.00	≤40
EGR+LB+OC+IFM	180	0.95	≤30
EGR+LB+TB+OC+IFM	180	0.95	≤30
3V+CLFI	290	0.90	≤10
3V+CLFI+AIR+OC	370	1.00	≤60
EGR+AIR+DTR	265	0.80	≤10
EGR+AIR+DC	405	0.90	≤80
EGR+PAIR+DC	420	0.90	≤80
EGR+AIR+DC+OC	455	1.00	≤70
EGR+PAIR+DC+OC	470	1.00	≤40

Discussion of Table 9-6

Systems

The 3V+CLFI and LB systems have reached their currently demonstrated lower levels of emission control capability. Dual catalyst systems could possibly be introduced at this level. The start catalyst may not be needed in a dual catalyst system if the reduction catalyst can perform this function effectively. IFM systems become more important at these NOx levels for all but dual catalyst vehicles. EGR is no longer capable of providing all of the NOx control. The fuel economy lost by retard control of NOx can be partially regained by the IFM which regains some engine-out HC control which was lost by using high EGR rates.

Cost

The lean burn systems are still initially inexpensive, but their fuel economy penalty cannot be overcome.

Fuel Economy

All systems are showing fuel economy losses from the .41 HC, 3.4 CO, 1.5 NOx levels. These losses would be recovered later in time as cold start HC control is improved and manufacturers gain expertise at these emission levels. There is no inherent reason that fuel economy penalties must exist at this or any other level of emission control.

H_2SO_4 Emissions

Sulfuric acid emissions are again subject to the previous IAIR discussion. Also the sulfuric acid emissions of dual catalyst systems are not well defined and may be lower than indicated in this Table.

Table D-7
Systems for 0.41 HC, 3.4 CO, 0.4 NOx for 1979-1980

System	Cost	Fuel Economy Factor	H_2SO_4 Emissions, mgm
EGR+AIR+3W+CL/FI+OC	400	0.90	100
EGR+IAIR+3W+CL/FI+OC	415	0.90	100
EGR+AIR+3W+CL/FI+OC +OC	445	0.95	170
EGR+IAIR+3W+CL/FI +MOD+OC	460	0.95	140
EGR+AIR+OC	405	0.80	100
EGR+IAIR+OC	400	0.80	100
EGR+AIR+OC+IFM	420	0.85	100
EGR+IAIR+OC+IFM	425	0.85	100
EGR+AIR+OC+IFM+OC	470	0.90	170
EGR+IAIR+OC+IFM+OC	485	0.90	160
EGR+AIR+IFM	305	0.85	130

. Discussion of Table 9-7

Systems

The number of system options is much reduced as only the remaining systems have 0.4 NOx potential. The RCB+AIR+EFM system (Questor system) has appeared because of its low NOx and potentially low sulfuric acid emission capabilities. EFM or CLFI are necessary for best fuel economy.

Cost

Nearly all system costs are now similar at about $420. The Questor system is most attractive in terms of initial cost, but not in fuel economy.

Fuel Economy Factor

The fuel economy factors are again reduced, but can probably be recovered later in time, if development is continued vigorously.

H_2SO_4 Emissions

Only the Questor system is extremely low in sulfuric acid emissions. This is expected because of the absence of an oxidation catalyst in the oxygen rich exhaust, but must be verified by vehicle testing.

9.3 Production Lead Time Considerations

The production lead times associated with automotive products in Figure 9-1* reveal that design approaches for the various emission

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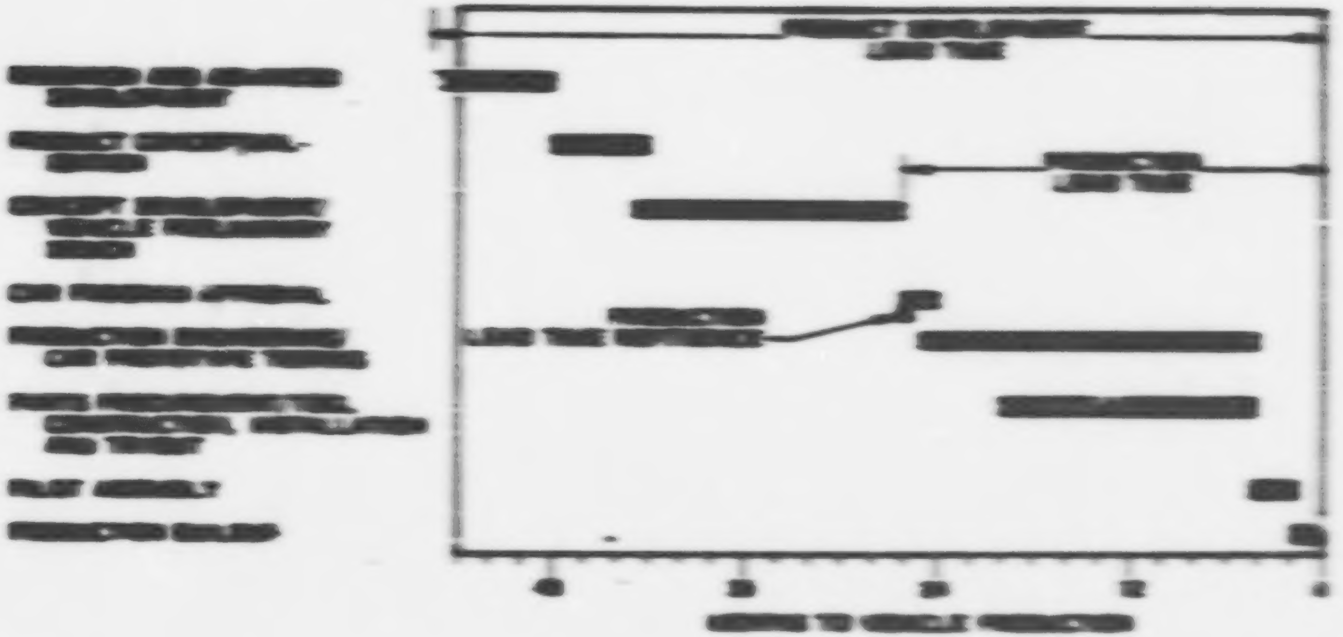
*See "Assessment of Domestic Automotive Industry Production Lead Time for 1975/1976 Model Years," Vol. I and II, December 15, 1972, prepared by the Aerospace Corporation under EPA Contract No. 68-01-0417.

Figure 9-1



Automotive Product Development Process

control systems to be manufactured by the vehicle manufacturer for 1979 should be completed by about July 1, 1976. This allows 25 months before the start of production about August 1, 1978 for the 1979 model year. The various vehicle manufacturers' estimates for individual components ranged from 24 to 39 months. Most of the control hardware in section 9.1 is manufactured by the vehicle manufacturers. Notable exceptions are the improved fuel metering (IFM), closed loop fuel injection (CLFI), and catalysts. These items are generally purchased from suppliers and require about 24 months or less from the date of order to full production. The only potential problem hardware in section 9.1 is the thermal reactors, and then only if they are not made by the vehicle manufacturer and are purchased from a supplier. The lead times in the casting industry are normally 36 months from the time of order to full production.

The emission control system selections for the 1979 model year have not been made by the vehicle manufacturers, but they should be made shortly after the sulfuric acid NPRM is published. Hopefully the Congress will also have clarified the gaseous emission requirements for 1979 by this time as well.

The vehicle manufacturers did not comment on the productivity of their specific development programs, but only one item discussed in section 9.1 seems to be lacking in development. This item is the improved AIR system (IAIR), and it is not expected to be a lead time problem as this is a modification to existing hardware and not a totally new development program.

9.2 Other Unregulated Emissions from Catalyst Vehicles

Unregulated emissions from catalyst equipped vehicles have been reported to include hydrogen sulfide, (H_2S), hydrogen cyanide, (HCN), along with carbonyl sulfide, (COS) and carbon disulfide, (CS_2), to name a few. With the exception of hydrogen sulfide, identifiable by the "rotten egg" odor, little characterization work has been done to date to determine the levels of the other unregulated emissions, or to characterize the amount of these emissions produced by non-catalyst equipped vehicles. Work is underway within EPA in this area currently, however.

It is concluded that the conventional gasoline engine, though characterized for emissions to a large extent, still needs additional characterization. Hydrogen chloride, hydrogen bromide, chlorine, bromine, vinyl chloride and other halogenated compounds have not been fully characterized from the conventional gasoline engine utilizing leaded fuel. Further, almost no data exist on the levels of hydrogen cyanide, nitrosamines, and organic sulfur compounds which could be emitted in trace quantities from non-catalyst cars.

Further characterization of oxidation catalyst systems needs to be done, and also dual and 3-way catalyst systems need to be studied. Additionally, characterization work must be done on lean burn, stratified charge, rotary, Diesel, and gas turbine engines, both in the baseline configurations and with control systems.

Hydrogen sulfide can be emitted from catalyst vehicles when they operate under rich conditions. Hydrogen sulfide has a characteristic odor at levels far below those associated with adverse health effects. Scattered reports have been received of hydrogen sulfide odor from in-use 1975 catalyst vehicles. EPA is still assessing the magnitude of this problem and what action can be taken to correct it. Preliminary indications are that the H_2S - emitting vehicles have improperly adjusted or defective emission control hardware which results in overly rich conditions into the catalyst. It is concluded that the H_2S problem should not get any worse than it is now and measures to improve vehicle maintenance or construction should reduce the incidence of occurrence.

The Bell Research Laboratories have identified hydrogen cyanide (HCN) in laboratory experiments intended to simulate vehicle catalyst systems and have suggested that HCN might be produced under certain conditions in sufficient quantities from catalyst equipped vehicles to present a health hazard. However, the Bell research was conducted as a laboratory test set-up rather than an actual vehicle test. In view of the effect of exhaust water content in suppressing HCN formation which was identified by Bell, there is substantial doubt that significant quantities of HCN are, in fact, produced by catalyst-equipped vehicles, although further work is desirable to confirm this.

Base metal catalysts such as the nickel alloy reduction catalyst being developed by Gould, Inc. emit certain metallic compounds. Metallic nickel has been identified and it is suspected that nickel carbonyl and nickel oxide could be emitted. Reduction catalysts using ruthenium may emit ruthenium oxide during oxidizing conditions.

Appendix IV provides a further discussion of unregulated automotive pollutants.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

[illegible]

OFFICE OF
AIR AND WASTE MANAGEMENT

Mr. Daniel [illegible]
Manager, Development Department
American Motors Corporation
14250 Plymouth Road
Detroit, Michigan 48232

Dear Mr. [illegible]:

Section 202(b)(4) of the Clean Air Act, as amended, requires the Environmental Protection Agency to review and report annually to the Congress on the progress being made in efforts to develop emission control systems needed to implement Federal motor vehicle emission standards established under Section 202 of the Act.

On March 5, 1975, EPA granted a one-year suspension of the effective date of the 1977 emission standards for exhaust emissions of hydrocarbons and carbon monoxide from light duty vehicles. That suspension was granted, even though it was found that oxidation catalyst technology exists which would permit the achievement of the standards by the statutorily required date, because the EPA Administrator concluded that such technology could not be considered "effective" under the terms of Section 202(b)(5) of the Act in view of the potential public health risk posed by emissions of sulfuric acid from cars equipped with such emission control systems, particularly when these systems were designed to achieve maximum degrees of control of hydrocarbons and carbon monoxide. In addition to granting the one-year suspension requested by auto manufacturers, the Administrator simultaneously announced EPA's intention to adopt a sulfuric acid emission standard applicable to light duty vehicles beginning with the 1979 model year and recommended Congressional action to further delay the imposition of more stringent exhaust hydrocarbon and carbon monoxide emission standards for light duty vehicles until suitable limitations on sulfuric acid emissions, as well as those of hydrocarbons and carbon monoxide, can be achieved.

As part of the reporting requirements of Section 202(b)(4), and in support of our efforts to develop and propose a suitable sulfuric acid emission standard for light duty vehicles, EPA is conducting an assessment of the status of efforts to achieve control of exhaust hydrocarbon and carbon monoxide emissions simultaneously with minimizing emissions of sulfuric acid. Accordingly, pursuant to Section 114(a)(1) of the Clean Air Act, you are requested to provide us with information regarding your efforts to characterize and control sulfuric acid emissions from light duty vehicles being designed to achieve various levels of hydrocarbon and carbon monoxide control. While this request is being made specifically for information regarding light duty vehicles, submission of relevant information on light duty trucks, if available, would also be appreciated.

The desired information, which is described in the enclosed outline, is divided into two main areas: a) data obtained by your company in characterizing sulfuric acid emissions from various types of light duty vehicle systems, and b) descriptions of your company's efforts and results in attempting to minimize sulfuric acid emissions while achieving stringent levels of hydrocarbon, carbon monoxide, and oxides of nitrogen control.

The information provided by your company should, in general, follow the enclosed outline. You may limit the information supplied in response to this request to that information which has not previously been supplied to EPA. However, if portions of the desired information have already been supplied to EPA, please indicate the appropriate documents by specific reference and supply copies of the earlier submissions if possible.

Your response should be submitted to EPA no later than September 2, 1975. Three copies should be submitted to:

Director, Emission Control Technology Division
Attention: Status Report Team
U.S. Environmental Protection Agency
Motor Vehicle Emission Laboratory
2565 Plymouth Road
Ann Arbor, Michigan 48105, USA

In addition, please provide two copies of your response to:

Deputy Assistant Administrator for Mobile Source Air Pollution Control
Attention: Mr. Joseph Merenda (AW-455)
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460

Except for information claimed by the submitter to be trade secret (the treatment of which is described in the enclosed [illegible]), a copy of each submission will be placed in a public docket and will be available for public inspection through the Freedom of Information Center at EPA Headquarters in Washington, D.C.

Questions concerning the data requested should be addressed to Mr. John DeKany, Director of the Emission Control Technology Division, which Division has primary responsibility within EPA for gathering and analyzing data on the status of technology for vehicle emission control. Also, staff from that Division may contact you for additional information or explanations, and such request should be deemed by you as an integral part of the request for data made by this letter.

While similar in format to requests made by EPA in previous years for information on the status of efforts to achieve standards for light duty vehicle hydrocarbon, carbon monoxide and oxides of nitrogen emissions, this request focuses specifically only on one aspect of the feasibility of achieving such standards, and of the costs which may be associated with doing so; namely, the impact of doing so without major increases in sulfuric acid emissions. As a result, this request does not address many other aspects of efforts in controlling currently regulated automotive pollutants, and a separate written request for information on these other areas may be anticipated later this year.

Your cooperation in assuring that the Environmental Protection Agency receives clear, detailed, and understandable information describing the efforts of your company in the characterization and control of automotive sulfuric acid emissions will contribute materially to ensuring the availability of a sound technical data base for future decisions on automotive emission control standards.

Sincerely yours,

/s/
Roger Strelow
Assistant Administrator
for Air and Waste Management (AW-443)

Enclosure

OUTLINE

FOR LIGHT DUTY VEHICLE SULFURIC ACID EMISSION CONTROL STATUS REPORT

The following outline should be followed in submitting the requested information. Any information not identified in the outline or the discussion of the outline that you feel is necessary for an accurate description of the technical efforts of your company to characterize and develop methods to control light duty vehicle sulfuric acid emissions may also be included:

I. Characterization of Light Duty Vehicle Sulfuric Acid Emissions

  A. Non-catalyst production vehicles
  B. Oxidation catalyst production vehicles
  C. Prototype non-catalyst vehicles
  D. Prototype oxidation catalyst vehicles
  E. Prototype advanced catalyst systems

II. Light Duty Vehicle Sulfuric Acid Emission Control Development Efforts

  A. Re-optimization of existing systems
  B. Catalyst modifications
  C. Air injection modifications
  D. Fuel metering modifications
  E. Advanced catalyst systems
  F. Sulfuric acid traps

III. Confidentiality of Trade Secret Information

DISCUSSION OF OUTLINE

The specific types of information requested for each item in the outline are discussed in more detail below.

I. Characterization of Light Duty Vehicle Sulfuric Acid Emissions

This section should present and discuss all data obtained by your company which help to characterize the quantities of sulfuric acid emitted by light duty vehicles designed to achieve various levels of HC, CO, and NOx control. Because of the difficulties in comparing bench test or engine dynamometer data with vehicle test data, only vehicle data are specifically requested in this section. However, if your company feels that certain bench or engine test data would be helpful in understanding or interpreting vehicle data, bench or engine test data may be included.

Vehicle characterization data should be organized according to the categories listed in the outline. These categories are discussed further below. Within each category, the data for each vehicle reported on should contain the information requested in Appendix A.

A. Non-catalyst production vehicles

This category includes all non-catalyst vehicles which were tested in the same configuration as vehicles certified for sale in the U.S. These vehicles may be either actual production vehicles, or may be certification prototypes. Any non-catalyst vehicles which have been modified in such a way that they could not be considered to be covered by an EPA certificate of conformity should be reported on in Section I.C., rather than in this category.

B. Oxidation catalyst production vehicles

This category includes all oxidation catalyst-equipped vehicles which may be considered production vehicles as defined for category I.A. above.

C. Prototype non-catalyst vehicles

This category includes all non-catalyst vehicles tested for sulfuric acid emissions which cannot be considered production vehicles as defined in category I.A. above.

This includes both conventional non-catalyst vehicles which have been modified from their production configurations and non-conventional systems such as stratified charge engines, vehicles equipped with special lean carburetion or other special fuel metering systems, or alternate engines such as gas turbine, Rankine cycle, Stirling, or Diesel engines, which do not employ catalytic exhaust treatment.

D. Prototype oxidation catalyst vehicles

This category includes all vehicles equipped with conventional oxidation catalyst systems but which do not fall into the production vehicle category I.B. This category also includes non-conventional engines equipped with conventional oxidation catalyst systems, such as a stratified charge engine with an oxidation catalyst.

E. Prototype advanced catalyst systems

This category includes all vehicles employing emission control catalysts in configurations other than the conventional single stage oxidation catalyst employed on many 1975 model light duty vehicles. This category would include start catalyst, three-way catalyst, and dual catalyst configurations.

II. Light Duty Vehicle Sulfuric Acid Emission Control Development Efforts

This section should provide a complete and detailed discussion of all efforts completed or presently in progress by your company to develop or evaluate various possible approaches to controlling sulfuric acid emissions from light duty vehicles. These efforts, which may include laboratory bench testing, engine dynamometer tests, and vehicle tests, should be discussed in the groupings identified in the outline. These groupings, and the specific types of data sought, are discussed more fully below:

A. Re-optimization of existing systems

This category includes efforts based on modification of various engine-catalyst system parameters without major changes in component design or system configuration. Examples of approaches included in this category are changes in engine calibration, catalyst size and location, air injection rate, etc.

B. Catalyst modifications

This category includes modifications to the chemical or physical structure of the catalyst such as changes in active material composition and loading, changes in catalyst substrate formulation or configuration, and changes in catalyst manufacturing and processing techniques, including the possibility of selective poisoning of SO_2 oxidation activity.

C. Air injection modifications

This category includes all modifications to pre-catalyst air injection systems other than simple changes in air injection rate or pump capacity. Included would be all types of air injection modulation, whether on-off or proportional to other engine or catalyst operating parameters.

D. Fuel metering modifications

This category includes changes in engine fuel-air metering other than simple changes in carburetor calibration. Included would be efforts to develop or evaluate various types of more accurate fuel-air metering devices such as electronic fuel injection, sonic flow carburetors, etc.

E. Advanced catalyst systems

This category includes all efforts involving major changes in catalyst system configurations such as dual catalysts, three-way catalysts, and oxidation catalysts operated at or near stoichiometric conditions either with or without catalyst oxygen level feedback.

F. Sulfuric acid traps

This category includes all efforts to develop or evaluate chemical or mechanical traps intended to remove SO_3 and/or H_2SO_4 from the exhaust stream leaving the oxidation catalyst, or SO_2 before the exhaust stream enters the catalyst.

In each of the categories discussed above, your company's efforts and results should be presented according to the following format:

1. Description of program

   Describe each approach being investigated in that category and discuss the technical rationale for pursuing that approach. If a given category has been eliminated from consideration on technical grounds, please discuss the data and judgments which have led to that conclusion.

2. Current status of program

   Discuss the current status of each of the efforts identified in item 1.

3. Experimental data

   Present and discuss all experimental data obtained to date from the efforts identified in item 1. for each category. See Appendix A for the information required from vehicle tests, Appendix B for engine dynamometer tests, and Appendix C for laboratory bench tests.

4. Cost estimates

   Provide any available estimates for the cost of implementing each of the approaches being investigated. Separate estimates for first cost and operating cost should be provided if possible.

5. Lead-time estimates

   Provide any available estimates of the lead-time which would be required to implement each approach on production vehicles.

6. Other impacts

   Discuss the impact of using each approach on other aspects of vehicle design and operation. If possible, the discussion should address each of the following items:

   a. Favorable or adverse impacts on ability to achieve control of HC, CO, and NOx to various levels.

b. Favorable or adverse impacts on vehicle fuel economy

c. Impact on emissions of other presently unregulated substances such as H_2S, catalyst or trap attrition products, etc.

d. Impact on vehicle safety, including consideration of effects on exhaust system temperatures, and

e. Any other impacts on vehicle manufacture or operation such as requirements for materials in limited supply, requirements of special fuels, relationships between sulfuric acid emissions and gasoline sulfur content for vehicles equipped with that control approach, need for periodic replacement or maintenance of system components, and any problems which might be posed by disposal of components such as chemical trapping materials or catalysts.

III. Confidentiality of Trade Secret Information

A. Information submitted in response to the request which accompanies this outline will be deemed to have been obtained pursuant to section 307(a)(1) of the Clean Air Act.

B. This means that only information which "...would divulge trade secrets or secret processes" may be kept in confidence. (Even this information will not be kept confidential in two situations: (1) when the information is emission data, or (2) if and when the information becomes "relevant" in any proceeding under the Act.) If you wish such information to be kept confidential prior to any proceeding, you must identify with particularity at the time of submission the data you regard as likely to "...divulge trade secrets or secret processes" if disclosed. Otherwise, such claims will be deemed to be waived. If confidential treatment of certain data is claimed at the time of submission you will be subsequently contacted by EPA and required to submit supporting information.

C. If the Administrator determines that a satisfactory showing has not been made that the information would disclose trade secrets or secret processes, you will be notified by certified mail. No sooner than 30 days following the mailing of such notice, any information with respect to which trade secret status has not been established will be placed in a public docket. Any information as to which the Administrator determines that a satisfactory showing has been made will be held confidential unless such information subsequently becomes relevant to a proceeding under the Act. In such case, a representative of your General Counsel's office will be notified in writing by certified mail and by telephone at least ten days prior to placing such material in a public docket.

Appendix A

Vehicle Sulfuric Acid Emission Data

All vehicle sulfuric acid emission data submitted to EPA should be in the following format and contain all of the requested information which is available. All 10 items should be submitted for catalyst cars. Items (2), (4), (5), and (6) do not apply to control systems not containing a catalyst.

(1) Vehicle manufacturer and model, vehicle mileage, inertia weight, and engine size should be listed. A complete description of the emission control system and of any non-conventional engine should be included. The type of air injection used (if any) should be described.

(2) For each catalyst employed, catalyst type, catalyst mileage, catalyst manufacturer, catalyst volume, active metal composition (e.g. Pt-Pd), active metal loading, amount of alumina on the catalyst, and catalyst space velocity (minimum, maximum, and nominal together with a description of the corresponding vehicle speed and load) should be given.

(3) The HC, CO, NOx, and CO2 emissions of the car over the FTP and over the condition of the sulfuric acid test should be listed. The emission design target of the vehicle (e.g. 1975 Federal) should be included. Also, fuel economy numbers in mpg should be listed for both the FTP and the EPA "Highway" test.

(4) The efficiency of the catalyst for control of HC, CO, and (if applicable) NOx emissions should be included (i.e., (engine-out minus tailpipe emissions) divided by engine-out emissions) as well as the conditions over which the efficiency was measured.

(5) The catalyst operating temperature over the sulfuric acid test (including the position of the thermocouple in the catalyst) should be given, as well as a description of the procedures used to provide catalyst cooling during the test.

(6) The oxygen levels at catalyst inlet and outlet during the sulfuric acid test should be listed.

(7) The type of mileage accumulation prior to the test should be given, including the fuel sulfur level used during mileage accumulation.

(8) The type of immediate preconditioning (e.g. Ann Arbor road route) before the sulfuric acid test, including fuel sulfur level, should be given.

(9) Particulate and sulfuric acid emissions (in g/mile and g/kilometer as H_2SO_4), the test cycle used, the sampling and analytical methods used, and fuel sulfur level should be given. Sulfuric acid emissions should also be normalized to 0.03% fuel sulfur. The percent conversion of fuel sulfur to sulfuric acid should be given.

(10) SO_2 emissions (in g/mile and g/kilometer) and percent recovery of total sulfur compounds should be given.

Appendix B

Engine Dynamometer Sulfuric Acid Emission Data

All engine dynamometer sulfuric acid data submitted to EPA should be in the following format and contain all of the requested information which is available. All 10 items should be submitted for catalyst-equipped engines. Items (3), (4), (5), (6), and (7) do not apply to control systems not containing a catalyst.

(1) Engine manufacturer and model should be listed. A complete description of the emission control system and of any non-conventional engine should be included. The type of air injection used (if any) should be described.

(2) For each catalyst employed, catalyst type, catalyst mileage, catalyst manufacturer, catalyst volume, active metal composition (e.g. Pt-Pd), active metal loading, amount of alumina on the catalyst, and catalyst space velocity should be given.

(3) The HC, CO, NOx, and CO2 emissions of the engine over the condition of the sulfuric acid test should be listed. The emission design target of the engine (e.g., 1975 Federal) should be included. Also, fuel consumption values should be listed for the test cycle.

(4) The efficiency of the catalyst for control of HC, CO, and (if applicable) NOx emissions should be included (i.e., (engine-out emissions minus catalyst-out emissions) divided by engine-out emissions) as well as the conditions over which the efficiency was measured.

(5) The catalyst operating temperature over the sulfuric acid test (including the position of the thermocouple in the catalyst) should be given, as well as a description of the procedures used to provide catalyst cooling during the test.

(6) The oxygen levels at catalyst inlet and outlet during the sulfuric acid test should be listed.

(7) The catalyst aging prior to the sulfuric acid emission test should be identified including data on the engine speed and load cycle used, hours accumulated over the cycle, catalyst operating temperature, inlet oxygen level, and fuel sulfur level. This information is especially important if the catalyst aging cycle is different from the sulfuric acid emission test cycle.

(8). The type of immediate preconditioning before the sulfuric acid test, including fuel sulfur level, should be given.

(9). Particulate and sulfuric acid emissions (in grams per test or g/mi), the test cycle used, the sampling and analytical methods used, and the fuel sulfur level should be given. Sulfuric acid emissions should also be normalized to 0.03% fuel sulfur. The percent conversion of fuel sulfur to sulfuric acid should be given.

(10). SO2 emissions (in grams per test) and percent recovery of total sulfur compounds should be given.

Appendix I

Laboratory Bench Test Sulfuric Acid Emission Data

All laboratory bench test sulfuric acid data submitted to EPA should be in the following format and contain all of the requested information which is available.

(1) Catalyst type, catalyst manufacturer, catalyst volume used in the test, active metal composition (e.g. Pt-Pd), active metal loading, and amount of alumina on the catalyst should be given.

(2) The complete composition, concentrations, and flow rate of the input gas should be given. The flow rate should also be given in terms of space velocity over the catalyst (bed volumes/hour). A description of the laboratory apparatus including source (bottle vs engine) of the gases and sampling and analytical methods should be given.

(4) The complete composition and concentrations of the output gas should be given.

(5) The catalyst temperature during the test should be given.

(6) The previous history and type of preconditioning for the catalyst should be given. This history should include the previous exposure of this catalyst to SO_2 and/or SO_3.

(7) The percent conversion of SO_2 to SO_3 as well as the percent recovery of total sulfur compounds should be given.

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APPENDIX II

SULFURIC ACID TEST PROCEDURES

This Appendix discusses the test procedures currently used by EPA to quantify light duty vehicle sulfuric acid emissions.

DRIVING CYCLE

The sulfuric acid driving cycle was derived from the CRC-APRAC CAPE 10 data on driving patterns in the Los Angeles area. The computer-generated cycle is designed to represent driving on congested urban freeways. This cycle is designed to simulate the type of potentially high localized sulfuric acid exposure situations about which EPA is concerned. The cycle has an average speed of 35 mph which is in accord with data showing maximum traffic flow on freeways at this speed. The cycle also contains long segments of 55 mph cruise along with periods of lower speed operation.

Initially, two different driving cycles were generated; each of which had an average speed of 35 mph, a 23 minute length, and represented congested freeway operation. The cycles were different in that they were composed of different sequences of driving modes. One cycle had an extended period (about 7 minutes) of 55 mph cruise toward the end of the cycle. The other cycle had shorter periods of 55 mph cruise interspersed throughout the cycle. Emission tests were run on both cycles and indicated no significant difference in sulfuric acid emissions for either cycle. The first cycle was selected for subsequent use in the EPA test procedure development program.

The driving cycle initially had speed fluctuations in 5 mph increments and did not have low magnitude-high frequency speed fluctuations (noise) characteristic of actual driving. Noise can result in higher HC and CO emissions as well as variations in exhaust oxygen level from the engine which could affect sulfuric acid emissions. Noise was added to the cycle creating a modified cycle. The maximum acceleration and deceleration rates on the cycle were then limited to 3.3 mph/second to be compatible with belt driven Clayton dynamometer being used by some of the automobile companies. These dynamometers cannot accommodate acceleration or deceleration rates greater than 3.3 mph/second. About 5 seconds of the 23 minute cycle were changed.

Some other very minor modifications may still be made in this cycle (as shown in Figure 1) to make it easier for drivers to follow with standard transmission cars. While none of the automobile companies have noted any problems in following the cycle, EPA engineers feel there may be minor problems with 3 or 4 speed standard transmission vehicles. If any modifications are made, they will be extremely minor and have little effect on emissions.

PRECONDITIONING

There are two categories of vehicle preconditioning that would affect sulfuric acid emissions in a certification-type program. The first is long term preconditioning which constitutes the mileage accumulation schedule for 4,000 miles for emission data cars and 50,000 miles for durability cars. The second is the immediate type of mileage or emission tests preceding the sulfate test itself. For example, the sulfuric acid test could be run immediately after the FTP in which case the FTP constitutes the immediate preconditioning. Current Federal emission test procedures for HC, CO, and NOx provide for long term

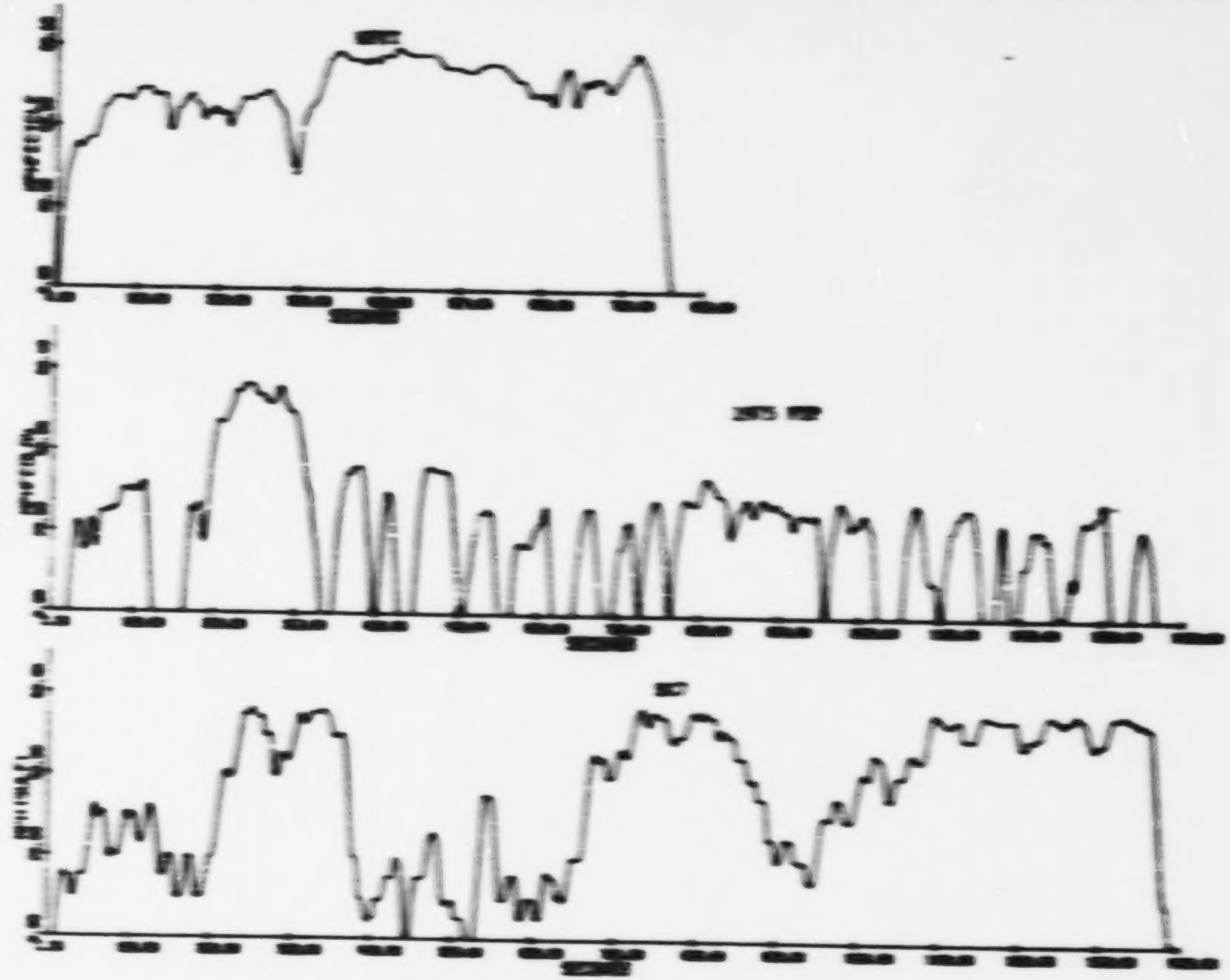

Figure 2: Comparison of the Three EPA Driving Cycles

mileage accumulation over the AMA driving schedule. The AMA schedule consists of running 11 laps around a 3.7 mile test track*. During each of the first 9 laps there are 4 stops with a 15 second idle. Normal accelerations and decelerations are used. In addition, there are five light decelerations each lap from the lap speed to 20 mph followed by light accelerations to the lap speed. The 10th lap is run at a constant speed (55 mph). The last lap is started with a wide open throttle acceleration from 0 to 70 mph followed by a second wide open throttle acceleration at the midpoint of the lap. The maximum speed for each of the 11 laps is listed below:

Lap	Maximum Speed, mph
1	40
2	30
3	40
4	40
5	35
6	30
7	35
8	45
9	35
10	55
11	70

A modified AMA schedule can also be used for mileage accumulation if the manufacturer wishes to do so. The modified AMA is identical to the regular AMA except that it has a maximum speed of 55 mph in the last lap instead of 70 mph. The wide open throttle accelerations in the last lap are retained. Both AMA mileage accumulation schedules have average speeds of about 30 mph.

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*Federal Register, Volume 37, No. 221, Part 85, Page 24318, November 15, 1972.

Not all of the automobile companies follow this schedule exactly since many companies do not have a 3.7 mile test track. EPA has given the automobile companies permission to make changes in this mileage accumulation schedule. However, all of the automobile companies follow schedules which are similar to the AMA cycle.

Sulfuric acid, stored on catalysts as aluminum sulfate at low catalyst temperatures associated with lower vehicle speeds, can be released at higher catalyst temperatures associated with higher vehicle speeds. Once these sulfates are purged from a catalyst, the catalyst is able once again to start storing. These phenomena are much more important for a pelleted catalyst which can contain up to 3000 g of alumina versus a monolith catalyst which contains about 100 g of alumina. However data from an EPA contract with Southwest Research Institute show that sulfuric acid storage and release is a relatively short term phenomenon for both monolith and pelleted catalyst vehicles. Southwest ran a variety of tests (FTP, SC, FET, steady state cruise) on different cars after AMA mileage accumulation and found complete recovery of total sulfur over the test sequence. Specific graphs showing this recovery of total sulfur is given in Figures 2-5 for the following four cars:

Plymouth - monolith catalyst, no air injection
Plymouth - monolith catalyst, air injection
Chevrolet - pelleted catalyst, no air injection
Chevrolet - pelleted catalyst, air injection

Data from EPA Contract 68-01-0497 with Exxon show that sulfuric acid emissions over an FTP for a pelleted catalyst preceded by 7 hours of 60 mph cruise are lower than sulfuric acid emissions over an FTP preceded by either the city or highway durability cycle developed by

Figure 1

Test No.	Test Type
1	Cold LA-4
2	Hot LA-4
3	SET-7
4	SET-7
5	HWFET
6	HWFET
7	Accel to 30
8	30 mph
9	Accel to 60
10	60 mph

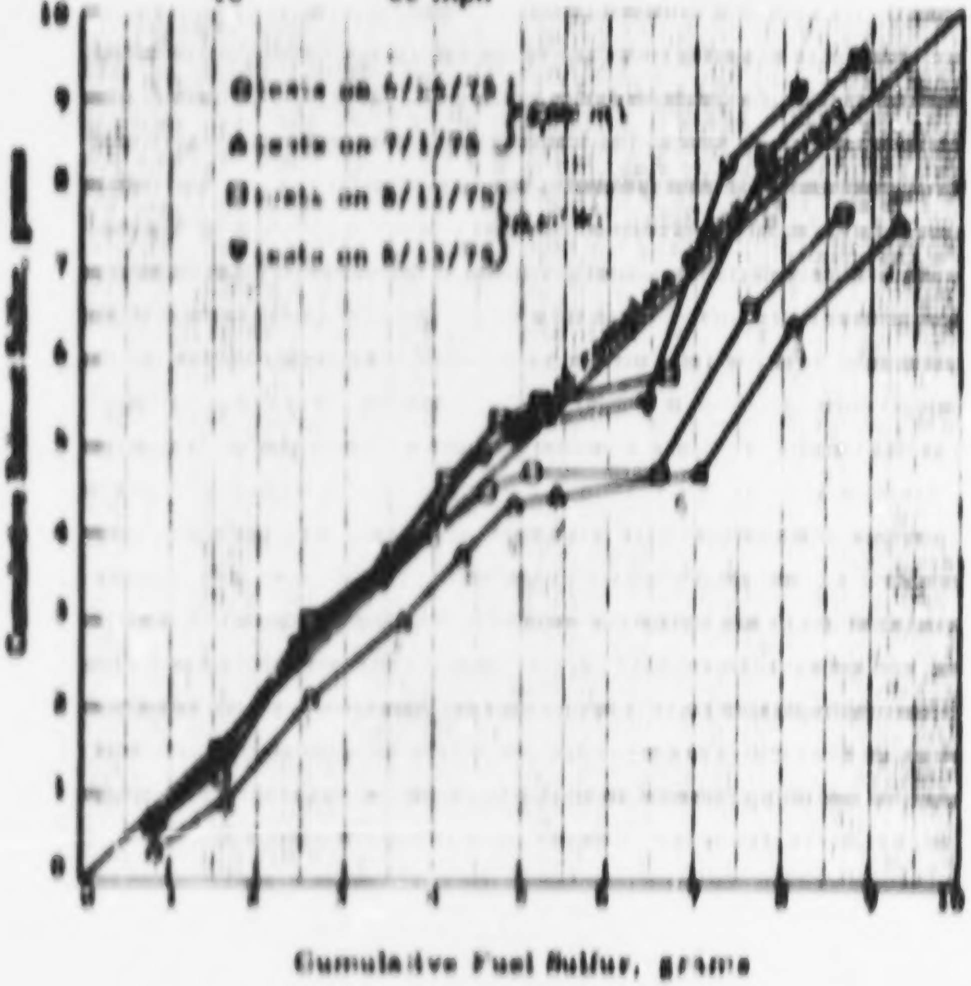

FIGURE 1. CUMULATIVE SULFUR RECOVERED IN EXHAUST AS A FUNCTION OF SULFUR CONSUMED WITH FUEL FOR A 1975 49 STATE PLYMOUTH GRAN FURY (SwRI Car EM-1)

Test No.	Test Type
1	Cold LA-4
2	Hot LA-4
3	SET-7
4	SET-7
5	HWFET
6	HWFET
7	Accel to 30
8	30 mph
9	Accel to 60
10	60 mph

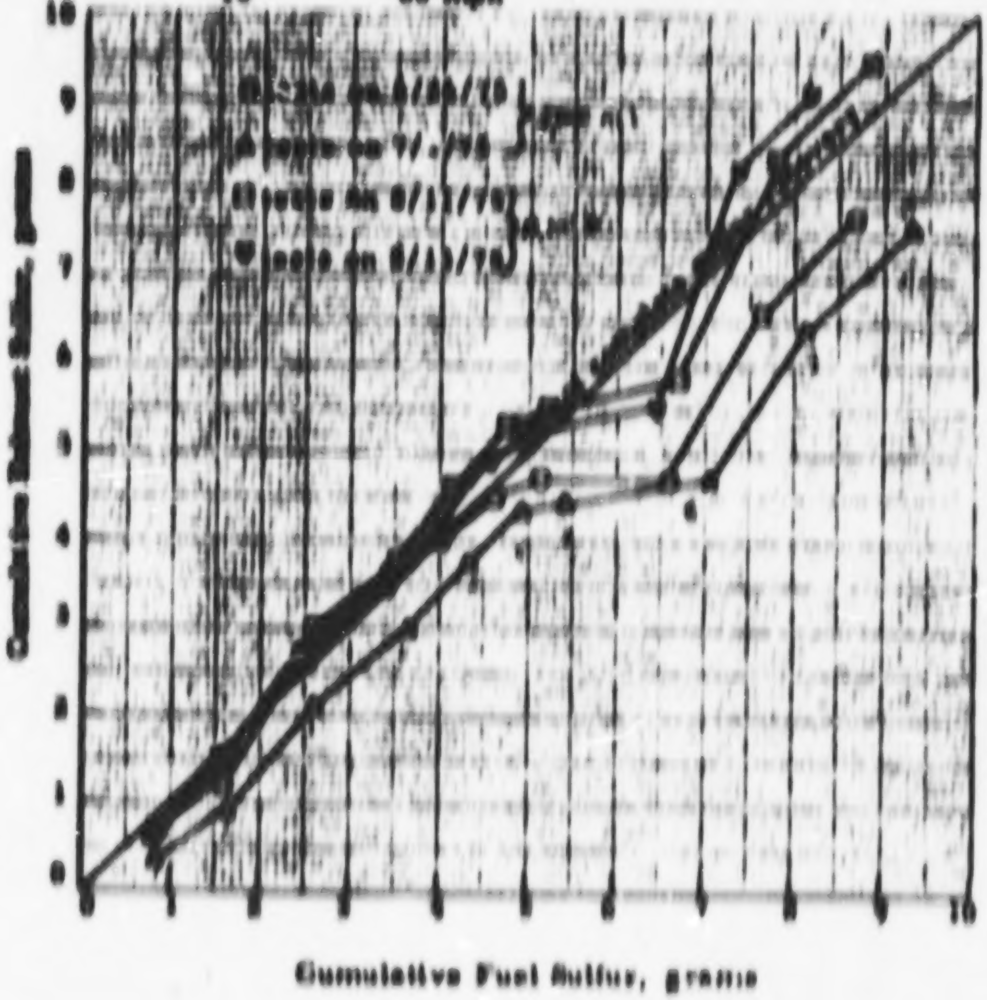

FIGURE 7. CUMULATIVE SULFUR RECOVERED IN EXHAUST AS A FUNCTION OF SULFUR CONSUMED WITH FUEL FOR A 1975 49 STATE PLYMOUTH GRAN FURY (SwRI Car EM-1)

TEST NO.	TEST TYPE
1	Cold LA-4
2	Hot LA-4
3 and 4	SET-7
5 and 6	HWFET
7	Accel to 30 mph
8	30 mph Steady
9	Accel to 60 mph
10	60 mph Steady

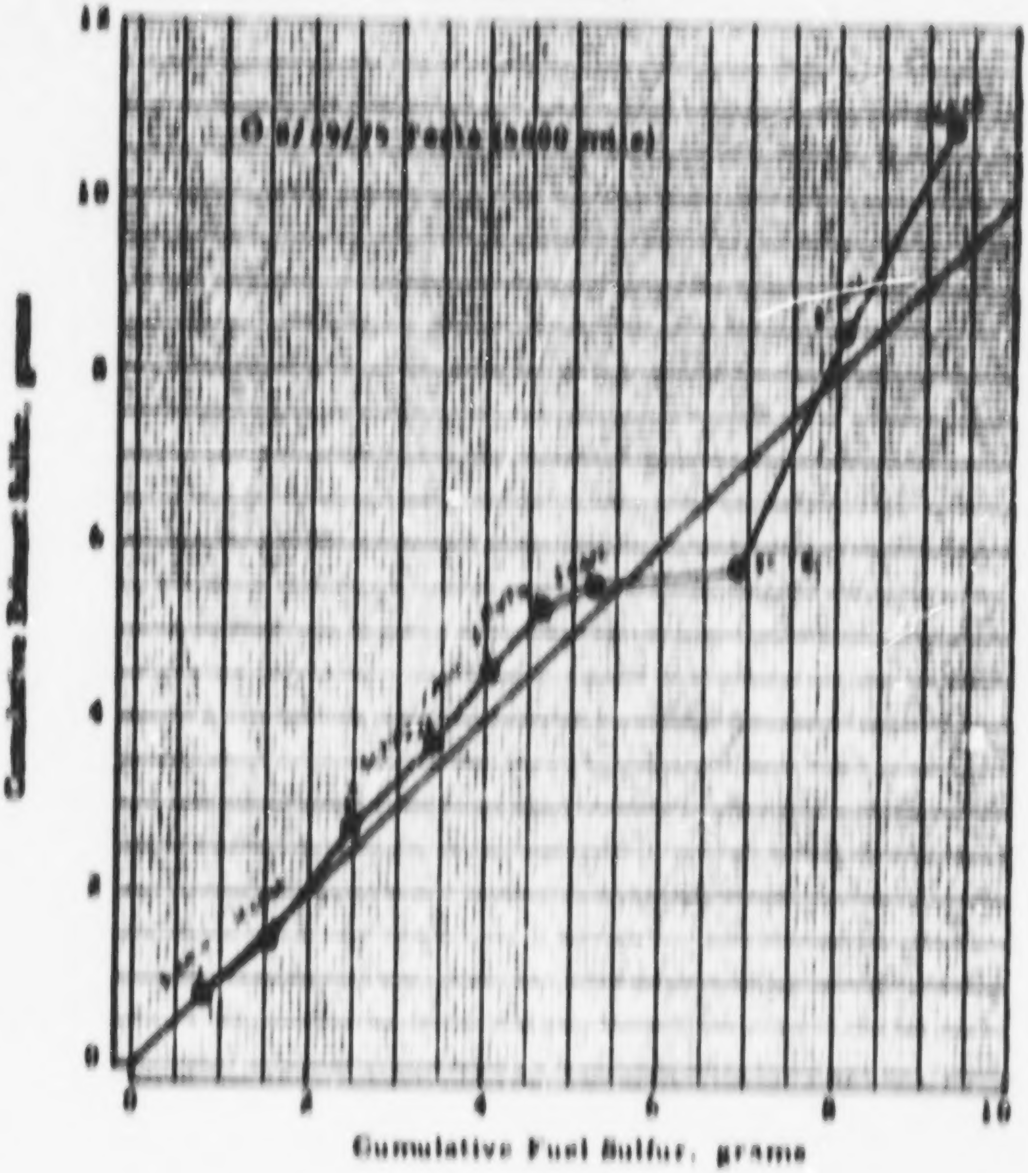

FIGURE 1. CUMULATIVE SULFUR RECOVERED IN EXHAUST AS A FUNCTION OF SULFUR CONSUMED WITH FUEL IN A 1975 49-STATE CHEVROLET IMPALA (SwRI CAR EM-2)
PELLETED CATALYST, NO AIR INJECTION

TEST NO.	TEST TYPE
1	Cold LA-4
2	Hot LA-4
3 and 4	SET-7
5 and 6	HWFET
7	Accel to 30 mph
8	30 mph Steady
9	Accel to 60 mph
10	60 mph Steady

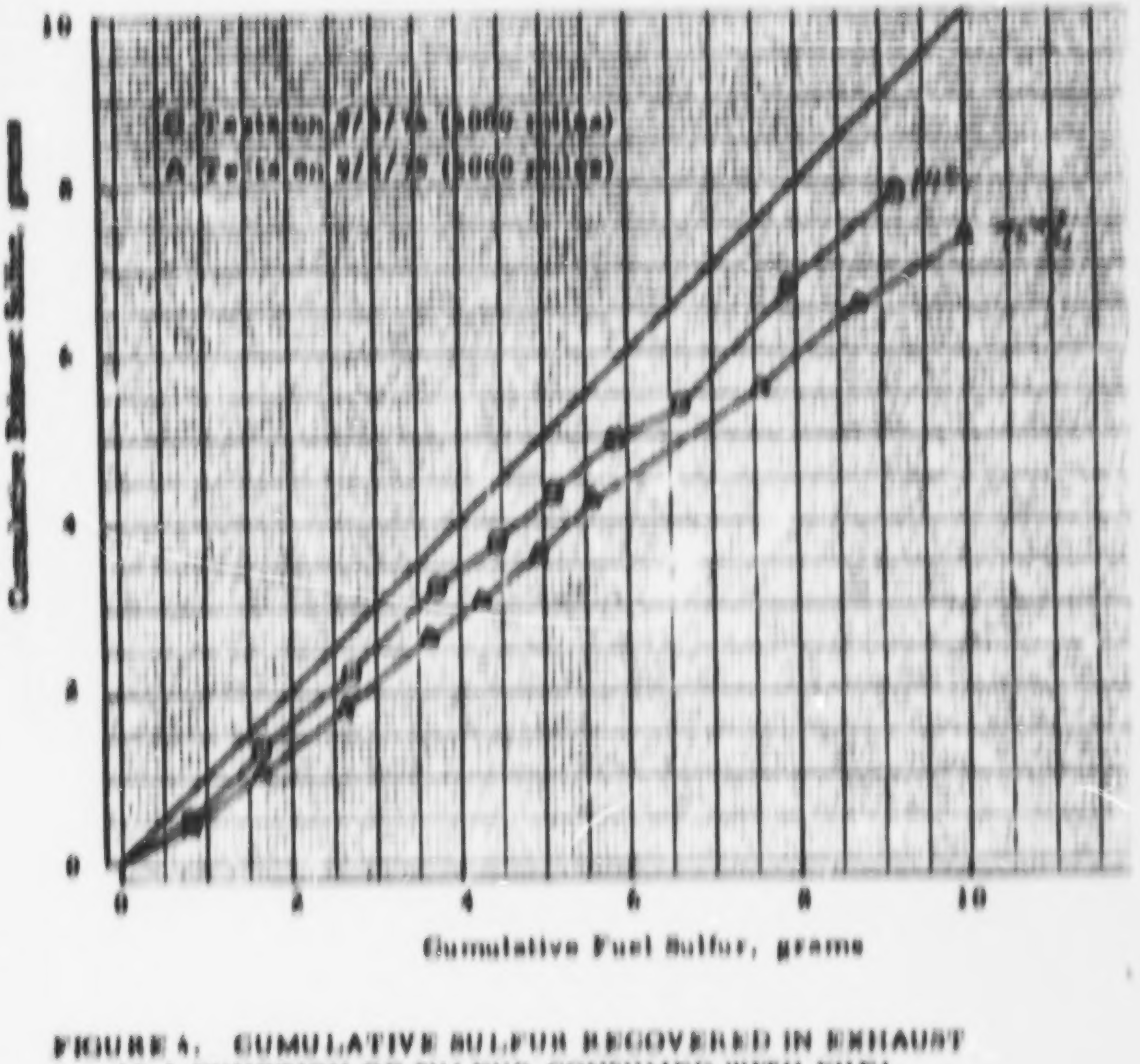

FIGURE 6. CUMULATIVE SULFUR RECOVERED IN EXHAUST
AS A FUNCTION OF SULFUR CONSUMED WITH FUEL
IN A 1975 CALIFORNIA CHEVROLET IMPALA
(SwRI CAR EM-4) PELLETED CATALYST WITH AIR INJECTION

TEST NO.	TEST TYPE
1	Cold LA-4
2	Hot LA-4
3 and 4	SET-7
5 and 6	HWFET
7	Accel to 30 mph
8	30 mph Steady
9	Accel to 60 mph
10	60 mph Steady

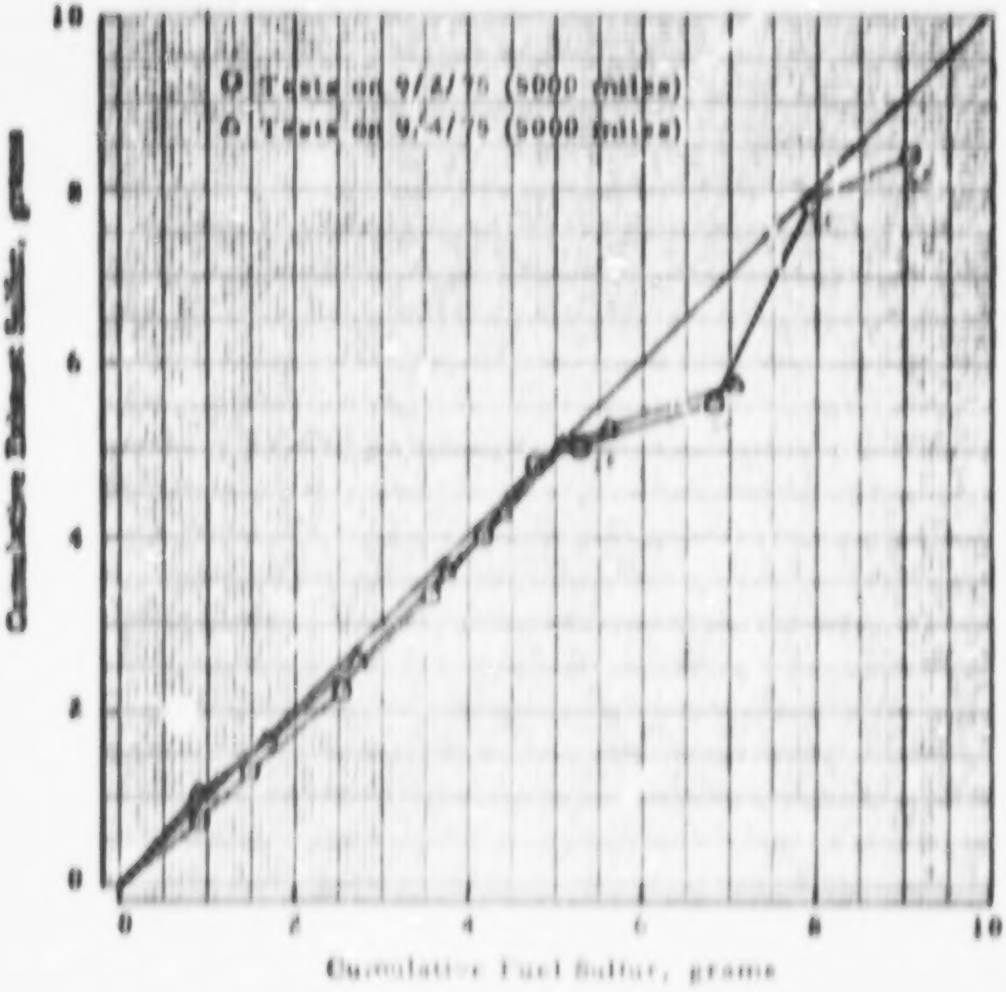

FIGURE 5. CUMULATIVE SULFUR RECOVERED IN EXHAUST AS A FUNCTION OF SULFUR CONSUMED WITH FUEL IN A 1975 CALIFORNIA PLYMOUTH GRAN FURY (SwRI CAR EM-3) MONOLITH CATALYST WITH AIR INJECTION

Exxon. These are not the similarly named EPA city and highway cycles. The average speed of the Exxon city durability cycle is 20 mph while the average speed of the Exxon highway durability cycle is 55 mph. It was also noted that sulfuric acid emissions over an FTP preceded by either the city or the highway durability cycle are essentially identical. Exxon found the following catalyst temperatures over these three types of preconditionings:

Exxon city durability cycle - 800°F
Exxon highway durability cycle - 1000°F
60 mph - steady state - 1200°F

The higher catalyst temperatures during the 60 mph preconditioning purged the catalyst of sulfuric acid stored at lower temperatures. This effect was not seen for the city versus highway durability cycle.

The first objective of the EPA test procedure program was to determine how modified versus regular AMA mileage accumulation affected sulfuric acid emissions. The second objective of the EPA test procedure program was to determine how immediate preconditioning (FTP, FET, etc.) affected sulfuric acid emissions over the sulfuric acid cycle.

EPA had the following four labs participate in the test procedure development program:

EPA-OMSAPC (Ann Arbor, Michigan)
EPA-ORD (Research Triangle Park, North Carolina)
Southwest Research Institute (San Antonio, Texas)
Exxon Research and Engineering (Linden, New Jersey)

Each lab tested one of the following four pairs of matched 1975 cars:

2 Fords, monolith catalyst with air injection

2 Chevrolets, pelleted catalyst without air injection

2 AMC Hornets, pelleted catalyst with air injection

2 Plymouth, monolith catalyst with no air injection

The Fords were designed to be sold in all 50 states for 1975 and meet both the 49 states (1.5 HC, 15.0 CO, 3.1 NOx) and California (0.9 HC, 9.0 CO, 2.0 NOx) standards. The other cars were designed for the 1975 Federal Standards

Each pair of cars was tested on the following test sequence.

1) Run AMA to 4,000 miles
(regular AMA, 11 laps, 70 mph maximum
speed)

2) SEQUENCE A
Ann Arbor road route - 1 hour
1 LA 4 (hot start)
4 hot start emission tests (HST)*
Ann Arbor road route - 1 hour
Overnight soak
Federal test procedure (FTP)*
Fuel Economy Test (FET)*

Repeat 2) twice for a total of three sequences

3) Run 500 miles of modified AMA**

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*HC, CO, NOx, sulfuric acid, and SO_2 measurements taken.

**55 MPH top speed, no wide open throttle accelerations.

4) **SEQUENCE B**

Ann Arbor road route - 1 hour
1 LA-4 (hot start)
Overnight soak
FTP*
SET - 3 times*
FET*

Repeat 4, twice for a total of three sequences

5) Repeat 3)

6) **SEQUENCE C**

Ann Arbor road route - 1 hour
1 LA-4 (hot start)
Overnight soak
FTP*
FET*
SET - 3 times*
Repeat 6, twice for a total of three sequences

7) Run SET as many times as necessary until a stable sulfuric acid emission value is obtained.

8) Repeat 3)

In addition, Sequence A was run again with modified preconditioning for the cars tested by EPA-OMSAPC and EPA-ORD.

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*HC, CO, NOx, sulfuric acid, and SO_2 measurements taken.

**55 MPH top speed, no wide open throttle accelerations.

The sulfuric acid emissions from the vehicles without air injection were low, about 1 mgpm. The vehicles with air injection had much higher sulfuric acid emissions, generally from 10 to 70 mgpm.

Summaries of the values obtained are given in Tables 1 through 8. These numbers generally show the FTP to have lower sulfuric acid emissions than either the sulfuric acid cycle or the FET. The FET was found to have higher sulfuric acid emissions than the sulfuric cycle. It is not currently known why the sulfuric acid cycle should give higher values than the FTP but lower values than the FET. Possibly sulfuric acid is stored more in the FTP, somewhat less over the sulfuric acid cycle, and less yet (if at all) over the FET. However, other factors such as kinetic limitations to the reaction at lower temperatures experienced in the FTP could be significant.

These values also show that the sulfate values for the sulfate cycles in sequence A are more variable than those in either sequence B or C. This greater variability is probably caused by lack of specific preconditioning since the Ann Arbor road route involves actual driving in city traffic which is not reproducible from run to run. The one LA-4 cycle for preconditioning is apparently insufficient to assure reproducible results. Also, supposedly identical cars (i.e. the two cars comprising a matched pair) did not give identical sulfuric acid values.

The values in sequences B and C are essentially similar. These numbers suggest that it does not seem to make any difference whether the sulfuric acid cycle is preceded by an FTP or an FET. This finding is encouraging since it allows EPA to place the sulfuric acid cycle after either cycle in the certification process. However, it must be noted

Table [illegible] SULFURIC ACID EMISSIONS OVER THE FTP

Lab	Vehicle	Catalyst		HC g/mile	CO g/mile	CO_2 g/mile	NO_x g/mile	SO_4 mg/mile	SO_2 mg/mile	MPG
EPA-A[2]	[illegible]	Monolith	Mean	.46	6.46	489.13	1.29	3.46	-	12.52
	[illegible]	oxidation	Std. Dev.	.08	.98	16.25	.128	1.26	-	.37
			Cf. Var.	12.85	20.28	2.32	9.99	36.32	-	2.98
EPA-ORD	[illegible]	Pellet	Mean	.51	8.35	876.26	2.06	.46	31.88	13.610
	Chevelle	w/o air	Std. Dev.	.09	2.33	40.72	.45	.23	6.25	.346
			Cf. Var.	17.21	27.72	4.65	25.60	50.75	20.15	8.76
[illegible]	Ply I & II	Monolith	Mean	.36	4.39	-	2.83	1.60	162.42	-
		oxidation	Std. Dev.	.15	1.60	-	.72	1.15	28.75	-
			Cf. Var.	41.62	36.38	-	25.51	70.32	17.79	-
GMR	AMC 5 & 6	Pellet	Mean	.63	5.41	-	2.82	15.41	68.89	-
		oxidation	Std. Dev.	.14	1.43	-	.60	7.37	65.59	-
			Cf. Var.	23.80	26.36	-	26.35	49.83	95.32	-

Table 2 SULFURIC ACID EMISSIONS OVER THE FTP

Lab	Vehicle	Catalyst		HC g/mile	CO g/mile	CO_2 g/mile	NO_x g/mile	SO_4 mg/mile	SO_2 mg/mile	MPG
EPA-C[2]	Dynamic	Monolith	Mean	.27	1.20	522.96	1.21	36.21	-	17.22
	Research	w/air	Std. Dev.	.03	.36	12.05	.121	17.77	-	.45
			Co. Var.	11.83	29.56	2.51	10.05	52.1	-	2.61
EPA-RTP	Chevrolet	Pellet	Mean	.26	7.60	626.76	1.33	.90	117.17	18.53
	Impala	w/air	Std. Dev.	.14	5.97	51.41	1.26	.42	22.60	.26
			Co. Var.	53.96	78.50	8.19	94.27	45.11	19.35	1.39
Exxon	Ply. I &	Monolith	Mean	.16	1.55	-	3.60	1.43	167.60	-
	II	w/air	Std. Dev.	.036	.90	-	1.30	1.14	18.29	-
			Co. Var.	19.47	61.35	-	36.06	76.38	25.93	-
SwRI	GMC 5 &	Pellet	Mean	.39	.30	-	2.65	73.56	65.63	-
	6	w/air	Std. Dev.	.02	.30	-	.92	30.43	26.70	-
			Co. Var.	24.60	106.6	-	36.29	41.40	36.05	-

Table 3: SULFURIC ACID EMISSIONS OVER THE [illegible] IN SEQUENCE A
[illegible]

Lab	Vehicle	Catalyst		HC g/mile	CO g/mile	CO_2 g/mile	NO_x g/mile	SO_4 mg/mile	SO_2 mg/mile	MPG
EPA-A[1]	Granada	Monolith	Mean	.32	1.53	551.6	1.36	29.62	-	15.99
	& Monarch	w/air	Std. Dev.	.03	.41	16.1	.14	9.88	-	.47
			Cf. Var.	10.58	26.27	2.93	10.40	46.83	-	2.9
EPA-ORD	Chevelle	Pellet	Mean	.44	14.76	686.8	1.90	.53	106.33	15.73
	& Impala	ox/air	Std. Dev.	.27	7.88	72.7	.43	.38	43.47	.51
			Cf. Var.	62.45	53.42	10.59	29.67	87.43	40.88	3.26
Exxon	Pty. I & II	Monolith	Mean	.11	1.35	-	2.72	1.52	126.98	-
		ox/air	Std. Dev.	.07	.89	-	1.06	1.31	33.97	-
			Cf. Var.	62.32	60.55	-	38.98	82.36	26.46	-
SWRI	GM 5 & 6	Pellet	Mean	.12	.28	-	2.12	54.57	66.57	-
			Std. Dev.	.02	.18	-	.14	22.81	15.51	-
			Cf. Var.	14.56	61.42	-	6.53	41.98	24.18	-

Table 4: SULFURIC ACID EMISSIONS OVER THE SETS IN SEQUENCE B
(SET PRECEDED BY FTP)

Lab	Vehicle	Catalyst		HC g/mile	CO g/mile	CO_2 g/mile	NO_x g/mile	$SO_4^=$ mg/mile	SO_2 mg/mile	MPG
[illegible]	Granada	Monolith	Mean	.31	1.96	562.85	1.33	25.80	-	15.7
	Monarch	w/air	Std. Dev.	.02	.58	11.7	.13	12.80	-	.36
			Cf. Var.	5.6	29.90	2.05	9.35	49.1	-	2.25
[illegible]	Chevelle	Pellet	Mean	.33	14.05	676.5	2.06	.47	-	-
	Impala	w/air	Std. Dev.	.13	6.93	49.91	.32	.26	-	-
			Cf. Var.	39.84	49.8	7.37	23.23	47.42	-	-
Exxon	Ply I & II	Monolith	Mean	.11	1.50	-	2.36	.75	125.66	-
		w/air	Std. Dev.	.05	.69	-	1.23	.63	31.30	-
			Cf. Var.	42.58	46.49	-	55.97	80.24	25.26	-
SWRI	GMC 5 & 6	Pellet	Mean	.11	.56	-	2.51	41.35	-	-
		w/air	Std. Dev.	.02	.36	-	.38	8.45	-	-
			Cf. Var.	16.4	66.95	-	14.60	21.80	-	-

Table 5: [illegible]

Lab	Vehicle	Catalyst		HC g/mile	CO g/mile	CO_2 g/mile	NO_x g/mile	[illegible] mg/mile	[illegible] mg/mile	[illegible]
[illegible]	[illegible]	Monolith	Mean	.38	1.90	304.55	1.29	18.15	-	16.2
	[illegible]	ox/air	Std. Dev.	.01	.31	11.05	.08	5.5	-	.36
			Cf. Var.	3.3	16.25	2.05	5.7	30.50	-	2.1
[illegible]	[illegible]	Pellet	Mean	.42	26.27	723.9	2.36	.36	76.00	14.53
	Impala	ox/air	Std. Dev.	.19	6.00	66.9	.56	.16	15.62	.56
			Cf. Var.	46.13	39.62	9.24	22.86	43.27	20.55	3.86
[illegible]	Ply. 2 & 11	Monolith	Mean	.10	.98	-	1.86	.86	115.63	-
		ox/air	Std. Dev.	.56	.47	-	.85	.40	11.42	-
			Cf. Var.	56.78	45.52	-	46.30	64.27	9.92	-
[illegible]	[illegible] 5 & 6	Pellet	Mean	.1	.11	-	2.37	39.35	61.12	-
		ox/air	Std. Dev.	.03	.08	-	.31	13.15	7.10	-
			Cf. Var.	21.25	54.50	-	13.10	32.75	1[illegible].25	-

Table [illegible]. SULFURIC ACID EMISSIONS FOR SULFURIC ACID CYCLES
[illegible] SEQUENCE A (4 SETS, FTP, [illegible])

Lab.	Vehicle	Catalyst		HC g/mile	CO g/mile	CO$_2$ g/mile	NO$_x$ g/mile	[illegible] mg/mile	[illegible] mg/mile	MPG
EPA-A^2	Granada	Monolith	Mean	.33	1.42	553.2	1.30	18.82	-	15.93
		w/air	Std. Dev.	.03	.25	12.1	.19	9.32	-	.30
			Cf. Var.%	10.10	17.70	2.9	14.56	49.50	-	2.30
EPA-A^2	Monarch	Monolith	Mean	.31	1.63	550.0	1.41	20.40	-	16.06
		w/air	Std. Dev.	.03	.57	20.1	.09	8.60	-	.60
			Cf. Var.%	11.05	34.76	3.66	6.63	42.56	-	3.71
EPA-[illegible]	Chevelle	Pellet	Mean	.43	10.25	606.0	3.21	.21	-	-
		w/o air	Std. Dev.	.33	6.96	72.7	.72	.26	-	
			Cf. Var.%	76.96	63.30	10.59	22.36	13.35	-	
EPA-[illegible]	Impala	Pellet	Mean	.46	19.36	-	.75	.86	106.33	15.73
		w/o air	Std. Dev.	.21	8.41	-	.13	.51	63.67	.50
			Cf. Var.%	.40	43.46	-	17.80	61.51	60.00	15.73
[illegible]	Ply-I	Monolith	Mean	.12	1.56	-	3.41	2.32	105.91	-
		w/o air	Std. Dev.	.06	.80	-	1.21	2.07	25.99	-
			Cf. Var.%	52.57	51.34	-	35.67	89.22	24.53	-
[illegible]	Ply-II	Monolith	Mean	.10	1.26	-	2.03	.72	148.03	-
		w/o air	Std. Dev.	.07	.98	-	.90	.54	41.95	-
			Cf. Var.%	72.07	86.95	-	44.32	75.56	28.36	-
[illegible]	39-5	Pellet	Mean	.11	.21	-	2.02	51.90	75.40	-
		w/air	Std. Dev.	.02	.09	-	.10	23.91	13.63	-
			Cf Var.%	14.73	43.55	-	4.75	45.99	18.08	-
[illegible]	39-6 ([illegible])	Pellet	Mean	.12	.35	-	2.22	57.15	57.73	
		w/air	Std. Dev.	.02	.27	-	.18	10.70	17.30	
			Cf. Var.	14.38	79.28	-	8.30	17.97	40.11	
[illegible]	39-5 ([illegible])	Pellet	Mean	.11	.21	-	2.02	51.90	75.40	-
		w/air	Std. Dev.	.02	.09	-	.10	23.91	13.63	-
			Cf. Var.%	14.73	43.5	-	4.75	45.99	18.08	-
[illegible]	39-6 ([illegible])	Pellet	Mean	.12	.35	-	2.22	57.27	57.73	
		w/air	Std. Dev.	.02	.27	-	.12	11.79	17.30	
			Cf. Var.%	16.39	79.28		2.30	37.97	30.11	

Table 7 SULFURIC ACID EMISSIONS FOR SULFURIC ACID CYCLES
OVER SEQUENCE C (FTP,SET, 2 SETS)

Lab.	Vehicle	Catalyst		HC g/mile	CO g/mile	CO_2 g/mile	NO_x g/mile	SO_4 mg/mile	SO_2 mg/mile	MPG
[illegible]	Granada	Monolith	Mean	.33	1.85	565.3	1.26	20.0	-	16.2
		w/air	Std. Dev.	.01	.21	9.2	.06	5.8	-	.27
			CV.Var.	2.70	11.40	1.70	4.60	29.1	-	1.70
[illegible]	Monarch	Monolith	Mean	.26	1.96	567.8	1.33	16.3	-	16.1
		w/air	Std. Dev.	.01	.40	12.9	.09	5.2	-	.41
			CV. Var.	1.80	20.90	2.40	6.80	31.90	-	2.50
[illegible]	Chevelle	Pellet	Mean	.34	10.27	723.9	3.36	.27	-	-
		w/o air	Std. Dev.	.17	3.71	66.9	.90	.10	-	-
			CV. Var.	49.85	36.12	9.24	26.99	36.10	-	-
[illegible]	Impala	Pellet	Mean	.45	22.26	-	1.33	.41	76.00	14.53
		w/o air	Std. Dev.	.19	9.60	-	.22	.21	15.62	.56
			CV. Var.	42.41	43.14	-	16.72	50.43	20.55	3.86
Exxon	Ply-I	Monolith	Mean	.09	.72	-	2.00	.48	116.49	-
		w/o air	Std. Dev.	.03	.20	-	.79	.40	6.50	-
			CV. Var.	41.20	38.34	-	39.65	82.07	5.58	-
Exxon	Ply-II	Monolith	Mean	.11	1.23	-	1.64	1.23	124.77	-
		w/o air	Std. Dev.	.08	.65	-	.90	.57	26.36	-
			CV. Var.	71.71	52.69	-	54.70	46.46	14.23	-
GMRC	GM-1 (GMRC)	Pellet	Mean	.10	.16	-	2.33	31.3	67.06	-
		w/air	Std. Dev.	.02	.14	-	.18	9.2	10.06	-
			CV. Var. %	15.00	88.70	-	7.80	29.40	15.00	-
GMRC	GM-4	Pellet	Mean	.10	.05	-	2.41	47.40	55.20	-
		w/air	Std. Dev.	.03	.01	-	.44	17.10	6.30	-
			CV.Var. %	27.50	20.30	-	18.40	36.10	11.50	-

Table 8 SULFURIC ACID EMISSIONS FOR SULFURIC ACID CYCLES OVER SEQUENCE 8 (FTP, 2 SETS, HFET)

Lab	Vehicle	Catalyst		HC g/mile	CO g/mile	CO_2 g/mile	NO_x g/mile	SO_4 mg/mile	SO_2 mg/mile	MPG
[illegible]	Granada	Monolith	Mean	.31	1.49	561.2	1.43	29.4	-	15.7
		w/air	Std. Dev.	.01	.19	13.6	.26	12.4	-	.39
			Cf. Var%	2.60	13.00	2.40	17.80	42.0	-	2.4
[illegible]	[illegible]	Monolith	Mean	.31	2.39	564.1	1.21	20.60	-	15.6
			Std. Dev.	.03	.47	9.8	.02	11.60	-	.29
			Cf. Var%	8.60	40.80	1.70	1.70	56.20	-	1.9
[illegible]	Chevelle	Pellet	Mean	.32	12.77	476.4	3.34	.24	-	-
		w/o air	Std. Dev.	.12	6.61	64.31	.87	.38	-	-
			Cf. Var%	36.51	51.71	7.37	25.98	13.56	-	-
[illegible]	Impala	Pellet	Mean	.31	15.71	-	.78	.70	-	-
		w/o air	Std. Dev.	.14	7.16	-	.26	.43	-	-
			Cf. Var%	43.16	45.86	-	20.47	61.27	-	-
Exxon	PIV-I	Monolith	Mean	.27	1.41	-	3.02	.36	134.35	-
		w/o air	Std. Dev.	.06	.80	-	1.26	.26	27.20	-
			Cf. Var%	50.29	56.60	-	41.78	96.79	20.25	-
Exxon	PIV-II	Monolith	Mean	.10	1.38	-	1.70	1.23	116.92	-
		w/o air	Std. Dev.	.03	.59	-	1.26	1.01	35.46	-
			Cf. Var.%	34.86	36.64	-	70.15	81.64	30.37	-
[illegible]	[illegible]	Pellet	Mean	.11	.12	-	2.68	31.0	-	-
	[illegible]	w/air	Std. Dev.	.03	.16	-	.68	7.1	-	-
			Cf. Var.%	25.86	11.43	-	22.80	23.1	-	-
[illegible]	[illegible]	Pellet	Mean	.10	.16	-	2.33	51.7	-	-
		w/air	Std. Dev.	.01	.01	-	.15	9.7	-	-
			Cf. Var.	4.30	82.51	-	6.60	18.8	-	-

that the data are extremely variable and may mask any differences between the three sequences.

Another finding from the limited data available is that sulfuric acid emissions are similar for cars preconditioned with either the regular or modified AMA. No statistically significant difference could be found between the two preconditionings.

However, the variability of the sulfuric acid data are high and greater than that found by EPA previously for HC, CO, and NOx over the FTP. Previous EPA work (SAE Paper 741035) found the following coefficients of variations for gaseous emissions over repetitive FTPs on a catalyst car:

HC	10%
CO	15%
NOx	2%
CO_2	4%

The reasons for the higher variability of sulfuric acid data are not known. It was thought that input emissions into the catalyst were not stable. Tests were run by Exxon, Southwest, and EPA-ORD in which continuous traces of HC, CO, NOx, CO_2, and sometimes O_2 were taken upstream of the catalyst. These emissions were found to be stable. Limited tests were run by EPA-OMSAPC in which SO_2 was measured continuously after the catalyst. These tests were done with an experimental second derivative spectrophotometer which is just in the process of being applied to automotive exhaust. The readings on this instrument are to be considered only preliminary until more exhaustive work is done. However, these readings showed that the instantaneous SO_2 emissions were not as reproducible as were the other gaseous emissions. This work suggests that sulfuric acid storage and release on the catalyst may cause poorer reproducibility. However, EPA feels the reproducibility of the cycle is acceptable for use in certification.

Another area that must be mentioned is that values obtained on the sulfuric acid cycle will frequently vary from one day to another. This variation is frequently as great as 100%. Yet repeating the sulfuric acid cycle on any given day can give stable values. For example, a Ford Granada tested by EPA gave stable sulfuric acid values of about 20 mgpm when tested one time and stable sulfate values of 12 mgpm when tested another time. While the reasons for this are not known, it is possible that the car itself is varying with time. This phenomenon is being investigated.

The data shown in Table 1, 2, 3, 4, and 5 exhibit variability greater than would be expected from conventional gaseous emission tests. The type of variability appears to depend on the emission control system. The variability for the vehicles equipped with air injection is much lower than the variability for the vehicles without air injection (w/o air).

The reason for this could be that the vehicles equipped with air (w/air) injection may have more repeatable oxygen levels in the exhaust. A comparison of variability of the data is shown in Table 8. Note that the variability is reduced for all pollutants HC, CO, NOx and H_2SO_4. The variability for CO exceeds the conventional test value by the greatest amount, indicating that there may be reason to explore the CO analyzer capability when operating with the high dilution rates typical of sulfuric acid testing. It is also possible that the variability is partly a function of emission levels and the cars emitting small quantities of sulfuric acid show great variability.

Table 9
Coefficient of Variation in Percent for Gaseous and Sulfuric Acid Measurements

Data Set	HC	CO	NOx	H_2SO_4
All Data	32.6	46.3	22.2	48.7
Table 3	39.2	52.4	19.3	52.0
Table 4	26.1	47.6	25.8	51.4
Table 5	31.8	38.9	21.8	62.7
all cars w/air	12.0	62.0	10.0	38.9
all cars w/o air	52.8	50.6	14.5	60.5
Conventional Testing	10.0	15.0	7.0	-

BASELINE PROGRAM

EPA is currently running a sulfuric acid baseline emission program on about 70 cars. This program is designed to provide emission factors on current cars and to measure emissions on advanced prototypes. The following categories of cars are being tested on this program.

(1) current non-catalyst cars
(2) catalyst vehicles designed for the following standards

HC	CO	NOx
1.5	15	3.1
1.5	15	2.0
0.9	9.0	2.0
0.4	3.4	2.0
0.4	9.0	1.5

(3) advanced non-catalyst systems (stratified charge, Diesel, lean burn, rotary)

(4) advanced catalyst concepts.

(5) fleet vehicles

Each catalyst car is being preconditioned on modified AMA for 500-1,000 miles with 0.03% sulfur fuel. The GM cars are being preconditioned on both modified and regular AMA to give EPA more data on the effect of these two preconditionings.

Each car is then being tested twice on the following sequence:

FTP

SC

SC

FET

SC

SC

Testing the car twice will give EPA information on the repeatability of the cycle and what preconditioning is necessary for a retest. The use of the FTP and FET before the sulfuric acid cycles will provide additional information on preconditioning. The baseline program will be complete in late 1975. The preliminary baseline data which were available prior to the completion of this report are included as Appendix V.

The data from the baseline program will enable EPA to properly place the sulfuric acid cycle in the certification process (i.e. after the FTP or FET).

Table 9. PLACEMENT OF THE SULFURIC ACID CYCLE IN THE CERTIFICATION PROCEDURE.

Current	Option 1	Option 2	Option 3
LA-4 (PreCond)	LA-4 (PreCond)	Cold LA-4 (PreCond)	12 hour soak (min.)
		SC	Cold LA-4 (PreCond)
		HFET	HFET
		SC	
12 hour soak (min)	12 hours soak (min)	12 hour soak (min)	12 hour soak (min)
Diurnal	Diurnal	Diurnal	Diurnal
FTP	FTP	FTP	FTP
Hot soak	SC	Hot soak	Hot soak
	Hot soak		
	HFET		
	SC		

APPENDIX III

Determination of Soluble Sulfates in CVS Diluted Exhausts: An Automated Method

The initial report that catalytic converters originally designed to reduce hydrocarbon and carbon monoxide emissions from late model automobiles also promote conversion of SO_2 to SO_3 or H_2SO_4 mist prompted a crash program to find or develop a fast and sensitive methodology for sulfates applicable to car exhausts. A number of analytical procedures for sulfates are described in the literature. Only a few of these, however, have the sensitivity sufficient to detect soluble sulfates in auto exhaust samples conveniently collectible within the time frame of the Federal Test Procedure.

The automated method described in this report is addressed primarily to the determination of water-soluble sulfates in CVS diluted exhausts from cars run on unleaded fuels. The method is quite general, however, and may be used for trace analysis of sample sulfates which can be leached out with water or aqueous alcoholic solutions.

The method, first developed elsewhere (1), is based on the reaction of sulfate ions with the solid barium salt of chloranilic acid (2,5 dichloro-3, 6-dihydroxy-p-benzoquinone). The reagent precipitates out $BaSO_4$ and releases highly uv absorbing acid chloranilate ions, the absorbance of which can be measured with a suitable spectrophotometer and related to sulfate concentration. The sensitivity of the method is greatly enhanced by conducting the reaction in a medium less polar than water, such as ethanol-water or isopropanol-water mixtures, where the solubilities of both $BaSO_4$ and barium chloranilate are reduced. The barium chloranilate method is estimated to have a limiting sensitivity for $SO_4^=$ to concentration levels of 0.06 µg/ml (8).

Cations are known to interfere negatively by reacting with the acid chloranilate to form insoluble salts. This interference is easily removed by passing the sample through a column of cation exchange resin in the hydrogen form. Anions such as Cl^-, Br^-, F^-, and PO_4^{---} interfere by precipitating out as barium salts with subsequent release of acid chloranilate ions. Some buffer systems are reported to minimize these anion interferences (1,5). For exhaust samples from cars run on nonleaded fuel, ionic interference was observed to be negligible when filtration on Teflon filters was used as a sample collection technique.

Sampling and Sample Preparation

Sampling methodology involves dilution of the auto exhaust with air in a dilution tunnel. At the temperature the tunnel is operated, SO_3 reacts readily with the available moisture in the exhaust to form H_2SO_4 mist. The acid aerosols are sampled through isokinetic probes and collected on 47 mm diameter 1 µ pore size Fluoropore® filters at flow rates of 28.3 liters per minute. The filters are extracted, preferably overnight, with 10 ml of 60/40 isopropanol/H_2O solution (60% IPA) in capped polyethylene bottles. Initial agitation until the filters collapse and completely submerge in the extracting solvent is conveniently accomplished by using a vortex test tube mixer. The supernatant extract can be analyzed directly in the automated sulfate instrument without further treatment.

The Automated Sulfate Instrument

A schematic of the principal components of the automated set-up is shown in Figure 1. Hardware requirements include:

a. Reservoir (LR) for the solvent mobile phase (80% IPA).

b. High pressure liquid pump (LP) capable of delivering liquids at flow rates of up to 1 ml/min at pressures as high as 1000 psi. Most liquid pumps used in high pressure liquid chromatography would be satisfactory.

c. Flow or pressure controller (FC).

d. Six-port high pressure switching valve (SV) equipped with interchangeable external loop (L).

e. Ultraviolet detector (D) equipped with appropriate filters or monochromator to isolate a narrow band of radiation centered at 310 nm.

f. Recorder to monitor detector response.

g. Automatic sampler (AS), such as the one used in a Technicon AutoAnalyzer set-up.

h. Peristaltic pump (PP), such as a Technicon proportioning pump, to draw sample into the sampling loop.

i. Cation exchange resin column (CX) - standard 1/4" O.D. x 10" gas chromatographic stainless steel column packed with analytical grade Dowex 50W-X2 (100-200 mesh) cation exchange resin in the hydrogen form.

j. Barium chloranilate column (BC) - standard 1/4" O.D. x 5" gas chromatographic stainless steel column packed with barium chloranilate suitable for sulfate analysis.

The operating principle of the automated instrument may be briefly described as follows:

Solvent mobile phase (50% IPA) in reservoir (SR) is continuously fed through cation exchange (CX) and barium chloranilate (BC) columns at flow rates of [illegible] by a high pressure liquid pump (LP). Background absorbance is continuously measured by a UV detector (D) at 310 nm and visually monitored in a strip chart recorder. A solenoid actuated, air operated switching valve (SV) is used for filling the external sampling loop (SL) with samples in conjunction with an automatic sampler (AS) and peristaltic pump (PP) and injecting the samples into the columns. At CX cations are removed and at BC anion reaction takes place. The $BaSO_4$ precipitate is retained in BC while the acid chloranilate is carried by the mobile phase through the detector system for colorimetric measurement.

For an automated sampling system such as shown in Figure 1, both SV and PP are electrically coupled to AS and controlled by electric timer relays such that both are activated whenever AS is sampling (i.e. L is being filled and mobile phase bypasses L). At the end of the sampling cycle, PP and AS stop and SV switches to the injection mode (i.e. mobile phase passes through L and carries the sample through US and BW columns).

For manual operation, SV may be retained or replaced by a similar switching valve equipped with an extended handle for manual switching. Samples may be introduced into the sampling loop by syringe injection or by peristaltic pump system similar to the one used in the automated version.

The automatic sampler (AS) used in our system is a Technicon AutoAnalyzer sampler with turntable capacity of 40 sample cuvettes. The cam programmer was replaced by two digital timers to allow flexibility in setting cycle times for the sampling-rinse operations.

Analytical Operation

Before the start of an analytical run, all components are switched to the operating mode, and SV, AS, and PP are allowed to cycle normally to clean out all components. During this time the sampling probe is immersed in a large reservoir of 60% IPA to prevent introduction of air into the system. Once a stable background absorbance is obtained, analysis of the samples proceeds. Sample cuvettes are filled with sample extracts and blank solutions (60% IPA) and then covered with thin polyethylene film to prevent evaporation losses. The filled cuvettes are arranged in the turntable according to the pattern blank,

blank, sample, blank, blank for concentrated samples and blank, sample, blank for dilute samples. Blanks are used to wash out the system between samples and minimize sample overlap. Depending on the size of the sampling loop and the mobile phase flow rate, cycle time can vary from 2.5 to 6 minutes per sample or blank. Analysis begins as soon as the sampling probe is returned to its normal position.

Calculation

A series of sulfuric acid standards in 50% IPA is normally run in the same manner as the samples, and a calibration curve, peak height vs. concentration, is plotted. Sample sulfate concentrations are calculated from the calibration curve. Total soluble sulfates in the filter $(SO_4^=)_F$ are calculated using the relation:

$$(SO_4^=)_F = (\mu g\ SO_4^=/ml) \times V_o \times d$$

where: V_o = total volume of original sample extract

d = dilution factor

= 1 if original sample extract was not diluted to bring detector response within range of of the calibration curve

Discussion

The solubilities of barium chloranilate and $BaSO_4$ vary with the isopropanol/water ratio in the mobile phase. A momentary imbalance in this ratio as a result of injection of a slug of sample or blank gives a negative background response if the injected slug is richer in isopropanol than the mobile phase, and a positive response if it is richer in water. To minimize this effect, we recommend that both the extracting solvent and the mobile phase for the analytical runs be taken from the same stock solution.

In order to determine the maximum absorbance of the acid chloranilate ions as they elute out of the barium chloranilate column of the automated system, the colored eluates corresponding to sulfate concentrations in the range 0 - 30 µg/ml were collected and scanned in a Cary 14 spectrophotometer. In this concentration range, peak maximum was observed at 310 nm. This corresponds to the isosbestic point reported by Schafer (3).

For isopropanol-water system, the volume of the mixture is not equal to the sum of original volumes of the individual components. In the case of a 60/40 isopropanol/water mixture, volume shrinkage on mixing is about 3.7%. This volume change should be taken into account when preparing standards or samples from aqueous solutions.

The working concentration range and sensitivity of the automated system depend on sample size. A degraded sensitivity better than 0.5 µg $SO_4^=$ per ml in 60% IPA was easily obtained using a 0.5 ml external sampling loop in conjunction with a duPont liquid chromatograph UV detector. Figure 3 shows a calibration run in the range 0-5 µg $SO_4^=$/ml using a 0.5 ml sampling loop with detector sensitivity set at 0.02 absorbance units full scale. The last two peaks, 4048 and 4049, correspond to exhaust samples from noncatalyst cars. Testing mode was the Federal Test Procedure. The calibration curve is non-linear with concentration and becomes flatter at the low concentration end. This is strongly suggestive of interplay of thermodynamic and kinetic effects. Similar behavior was likewise observed at the high concentration end.

Reproducibility of repetitive measurements is quite good. Table I shows the precision obtained for five repetitive scans of sulfate standards at concentrations of 1, 2, and 4 μg/ml. A 0.5 ml sampling loop was used.

Two experiments were conducted to determine the extractability of sulfuric acid from and absorption in Fluoropore filters. In the first of these, known amounts of sulfuric acid in 60% IPA were deposited on the filters and allowed to dry overnight. The filters were then extracted with 60% IPA and analysis of the liquid after the filters equilibrated with the solution overnight. The results show that extraction is quantitative and that the filter has practically no affinity for the solute. These results are summarized in Tables II and III.

Table IV shows the efficacy of the collection technique for trapping sulfuric acid aerosols. The aerosols were generated using a Collison aerosol generator, and then fed into the CVS dilution tunnel under conditions simulating a test run. The aerosols were collected through isokinetic probes and collected on Fluoropore filters. The back-up glass fiber filters used in these runs did not gain measurable weights, indicating no significant breakthrough of the collected particulate from the primary collecting filters.

Figure 3 shows a typical analytical scan of extracts from exhaust samples from cars run on nonleaded fuel. The first five peaks are sample peaks, while the next six are calibration peaks corresponding to concentration range 0-8 ug $SO_4^=$/ml. As a general rule, calibration runs are always made for each series of samples, as peak height-concentration relation may change as flow rate, back pressure, and column permeability vary over an extended period. This practice may be dispensed with for systems equipped with integrators.

Table V shows typical results of analysis for soluble sulfates of nonleaded exhaust samples collected on Fluoropore filters using the Federal Test Procedure. The low sulfate results correspond to test runs with noncatalyst cars and the high results to test runs with catalyst equipped cars.

A few filter samples were analyzed sequentially by x-ray fluorescence technique and by the barium chloranilate method. The filters were first analyzed by x-ray fluorescence, then extracted with 60% IPA and analyzed for sulfate in the automated instrument. The results are summarized in Table VI. Considering the fact that sample handling techniques were not closely monitored, agreement between the two methods is encouraging.

Conclusion

The automated method described in this report offers a sensitive (less than 0.5 μg $SO_4^=$ per ml), fast (less than four minutes throughput time from initial sample injection into the column), and convenient method for the analysis of soluble sulfates in auto exhaust. Sample preparation is minimal, as this involves only simple extraction with 60% IPA. There are no precipitates to cause deterioration of the optical cell, as the $BaSO_4$ precipitate is effectively retained in the barium chloranilate reactor column. Although primarily addressed to trace sulfate analysis of auto exhausts from cars run on nonleaded fuels, the method may be adapted to any sulfate sample which can be leached out with water or aqueous alcoholic solution.

Table I

Precision of Repetitive Measurements

Peak Height

$(SO_4^=)$ in µg/ml	1	2	5
	9.7	21.2	47.8
	9.9	20.4	48.8
	9.6	21.5	49.5
	10.2	20.1	48.6
	8.8	21.2	49.0
Mean	9.6	20.9	48.7
Standard Deviation	± 0.5	± 0.5	± 0.6
Coefficient of Variation	5.2	2.4	1.2

Table 11

Recovery of Deposited H_2SO_4 on Fluoropore Filters by Extraction with 80% IPA

Total µgs $SO_4^=$ on Filter	
Deposited	Found
10	10
20	20.5
30	30
40	40.5
50	50
60	60
169	172
338	350
507	494

Table III

Absorption of H_2SO_4 in 80% IPA by Fluoropore Filters

Total μgs $SO_4^=$ in Solution	
Initial	**Final**
10	10.5
20	20
40	40.8
60	61.2
200	205
400	392

Table IV

Collection of Generated H_2SO_4 Aerosols Fed into the CVS Dilution Tunnel

Sample #	Mass Loading in μgs	Total $SO_4^=$ on Filter in μgs	% $SO_4^=$ on Filter
4001-3	956	560	58.6
4002-4	1791	664	37.1
4003-2	1076	390	36.2
4004-1	1323	217	16.4
4005-3	2403	856	35.6
4006-3	206	115	55.8
4007-1	468	197	42.1
4008-2	21181	8438	39.8

Table V

Typical Results of Sulfate Analysis of Nonleaded Exhaust Samples Collected on Fluoropore Filters

Sample #	Mass Loading in μgm	Total $SO_4^=$ in μgm	% $SO_4^=$ as % Mass Loading
4034-1	415	20	4.8
4035-1	271	15.5	5.6
4036-1	252	16.7	6.6
4037-1	151	11	7.3
4038-1	120	10.8	9.0
4039-1	307	10.5	3.4
4076-1	232	84	36.2
4079-1	308	106	34.4
4080-1	430	192	44.6
4084-1	506	241	47.6
4087-1	765	316	41.3

Table VI

Soluble Sulfate Analysis: Preliminary Comparison of X-Ray Fluorescence and Barium Chloranilate Method (BCM)

Total $SO_4^=$ on Filters in μg

Sample #	Mass Loading	X-Ray Fluorescence Low Resolution	X-Ray Fluorescence High Resolution	BCM	Ratio X-Ray/BCM
4006	459	300	-	316	0.950
4007	379	184	-	173	1.064
4014	398	143	-	156	.917
4017	285	37	-	44	.841
4021	390	142	-	113	1.256
4032	1065	298	-	248	1.202
4036	224	-	12.8	9.8	1.306
4038	84	-	17.0	7.8	2.179
4039	250	-	12.4	9.8	1.265
4050	300	-	18.0	13.7	1.314

References

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3. Schafer, H. N. S., "An Improved Spectrophotometric Method for the Determination of Sulfate with Barium Chloranilate as Applied to Coal Ash and Related Materials," Anal. Chem. 39, 1719 (1967).

4. Barton, S. C. and McAdie, H. G., "An Automated Instrument for Monitoring Ambient H_2SO_4 Aerosol," In Proceedings of the Third International Clean Air Congress, Dusseldorf, Federal Republic of Germany, 1973, VDI-Verlag GmbH, 1973, p. C25.

5. Gales, M. E., Jr., Kaylor, W. H. and Longbottom, J. E., "Determination of Sulphate by Automatic Colorimetric Analysis," Analyst 93, 97 (1968)

FIGURE 1

FLOW SCHEMATIC FOR AUTOMATED SULFATE INSTRUMENT

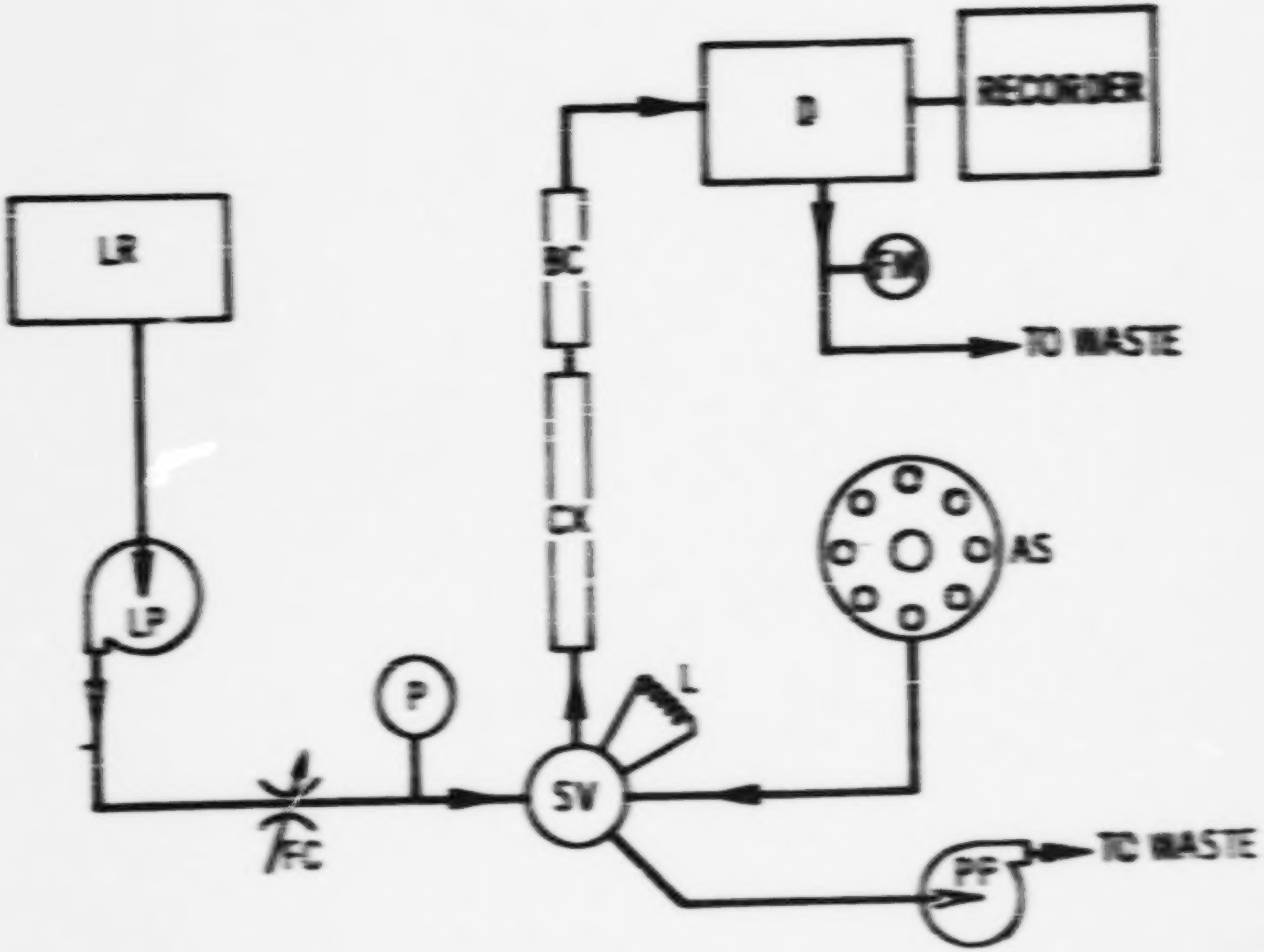

LR
LP
FC
P
SV
L
CX
BC
D
RECORDER
FM
TO WASTE
AS
PF
TO WASTE

Figure 1

Flow Schematic for Automated Sulfate Instrument

LR - Liquid reservoir
LP - High pressure liquid pump
FC - Flow or pressure controller
P - Pressure monitor
SV - High pressure switching valve
L - External sampling loop
CR - Cation exchange resin column
BC - Barium chloranilate column
D - UV detector
FM - Flow monitor
AS - Automatic sampler
PP - Peristaltic pump

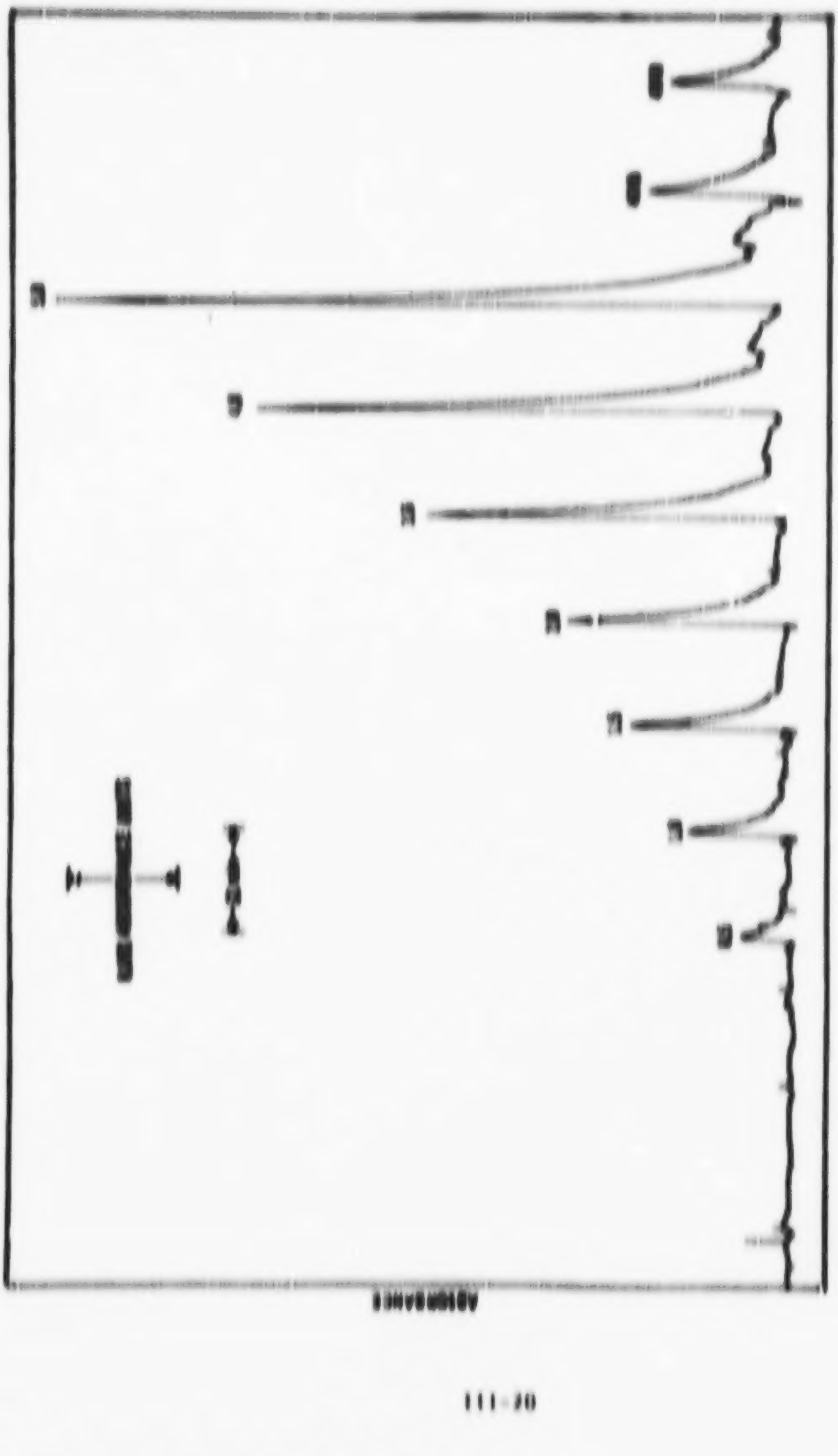
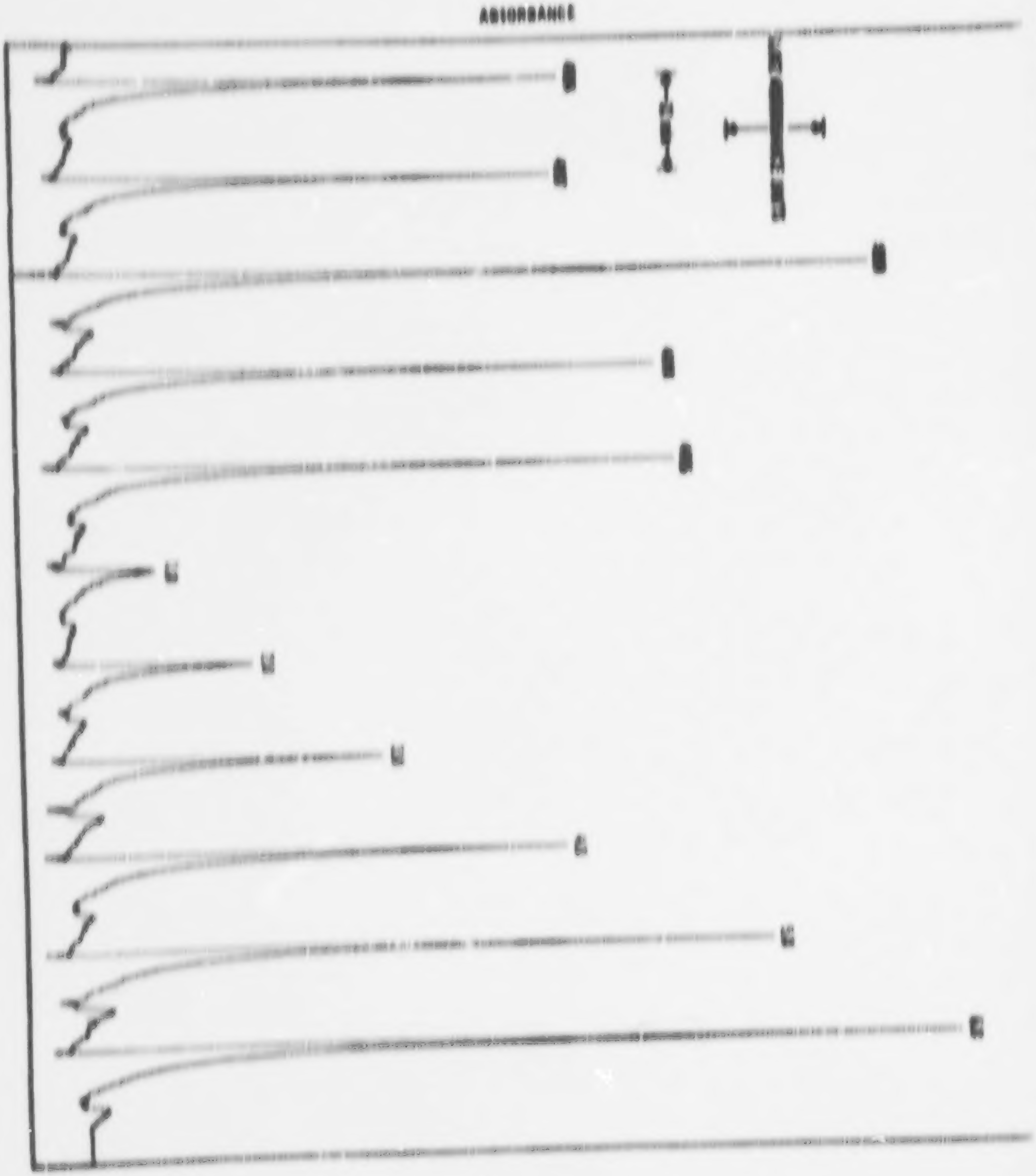

ABUNDANCE

Figure 8

Sulfate calibration for concentration range 0-5 μg $SO_4^=$ per ml in 80% IPA. 4048 and 4049 are exhaust samples from a car not equipped with catalyst.


ABSORBANCE

File
6.2.9

Non-Regulated Emissions from Light-Duty Motor Vehicles

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Health Effects Research Laboratory
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Environmental Protection Agency
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October 1976

INTRODUCTION

The statutory light-duty vehicle emission standards for hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NO_x) embodied within the 1970 Clean Air Act Amendments and concern regarding the public health consequences of emissions resulting from the use of lead additives in gasoline have been until recently, the principal motivating forces which have influenced the research efforts by both the EPA and industry with regard to emissions characterization.

The effect of fuel composition, fuel additives, engine parameters, and post-combustion emissions control devices on regulated emissions (HC, CO, and NO_x) has constituted the bulk of the emissions characterization effort with the internal combustion engine (ICE) which has been the basic automotive powerplant for the past several decades. The fact that the hydrocarbon emissions standards were based, not upon direct public health effects of hydrocarbons, but rather upon the role hydrocarbons play in atmospheric reactions to form oxidants resulted in substantial effort to characterize the individual hydrocarbon species emitted and to further define their "reactivity." The Congressional concern about lead in gasoline, which surfaced in the 1960's, caused the first real effort to examine non-regulated emission products from automotive engines. This resulted in programs which provided emissions characterization of exhaust particulates and exhaust lead compounds. These studies were expanded in the late 1960's to examine the effect of fuel composition, particularly increased aromatic content which is required to achieve equivalent octane quality when lead is removed from the fuel, on exhaust particulate, polynuclear aromatic hydrocarbons (PNA's), and phenols.

Section 211 of the 1970 Clean Air Act Amendments permits the EPA to restrict or prohibit the use of fuels or additives whose emission products endanger the public health or welfare or significantly impair the performance of emissions control devices. As a result, the EPA undertook major research programs to examine the effect of fuel composition and fuel additives on a broad range of emission products, both regulated and non-regulated. While these programs have focused principally upon gasoline-fueled light-duty ICE-powered vehicles, the exhaust generation, collection, and analysis techniques developed have begun to be applied to other powerplants, principally, the diesel engine. These programs have focused upon both regulated emissions (HC, CO, and NO_x) and these non-regulated emissions products: individual hydrocarbon species, PNA's, particulates, organic particulates, lead compounds, aldehydes, oxygenates, phenols, trace metals, sulfur compounds, and nitrogen compounds. The latter two general classes of emission products are only now beginning to be capable of analysis.

As a result of the initial thrust of these efforts, the ICE is currently the best characterized engine with regard to exhaust products. This is not to say that such engines have been fully characterized, as is evident from the recent concerns regarding the potential emission of ethylenedibromide (EDB), recently discovered to be a carcinogen. Only one very limited study has sought to determine the form of halogen emissions from ICE's burning leaded gasoline. Nonetheless, the ICE characterization data base must serve as the benchmark against which to judge the public health trade-offs associated with non-regulated emission products from advanced emission-controlled ICE's, alternate ICE powerplants, alternate fuels, and new fuel additives. At this time, only a qualitative comparison can be drawn, principally due to the critical lack of emissions characterization data from advanced emission-controlled ICE's and alternate engines.

Table 1 presents this qualitative comparison of non-regulated emissions, known or estimated, for advanced emission-controlled ICE's and the diesel, rotary, Stirling, Rankine, and turbine alternate powerplants. The basic ICE serves as the basis for comparison. Table 2 summarizes the toxicological properties of many of the identified non-regulated pollutants while Table 3 presents specific compound identifications for the PNA, phenol, and aldehyde groups of compounds identified in ICE exhaust.

CATALYSIS

The use of oxidation catalysis has resulted in significant decreases in the emissions of HC and CO and of many non-regulated pollutants of public health concern (PNA's, aldehydes, phenols). Because these systems require the use of unleaded fuel, lead particulate emissions from vehicles so equipped have essentially been eliminated. In addition, because of the reaction characteristics of the catalytic process, the higher molecular weight hydrocarbons are disproportionately decreased resulting in the emission of lower molecular weight, less reactive, hydrocarbons. However, use of oxidation catalysts has also resulted in a significant increase in the emissions of an oxidized sulfur compound, sulfuric acid, to the extent that the principal exhaust particulate species from catalyst-equipped vehicles is sulfuric acid and the related bound water.

Reduced forms of sulfur, H_2S principally with traces of COS and CS_2, have been identified when such catalysts are operated under reducing (fuel rich) conditions. While fairly well characterized when operating within design limits, oxidation catalyst-equipped vehicles have not been well characterized outside of the design limits, although such operation may occur in the hands of the consuming public.

Noble metal (platinum, principally) attrition products from catalysts, earlier identified from prototype systems, now appear to be undetectable in particulate smaller than 10 microns. Larger particulate attrition products do, however, contain measurable quantities of such metals. Because of the severe lack of toxicological data available and because platinum has been shown to methylate, EPA is conducting extensive toxicological programs to assess the potential of public health risk associated with platinum exposures.

Dual catalysts and three-way catalysts might generally be expected to generate non-regulated emission products similar to those from oxidation catalysts, although in differing quantities. However, qualitative differences could result either from the more stringent reducing conditions associated with the NO_x reduction catalyst of the dual catalyst system, or from attrition products if non-noble metal catalysts are used. The potential for new or higher emission rates of non-regulated pollutants than from oxidation catalysts cannot be dismissed, however, particularly when such systems operate outside design limits. Such systems have not been well characterized, even when operating properly, let alone when operating outside limit targets.

Lean burn and stratified charge engines, when operated with gasoline, appear basically to emit both regulated and non-regulated pollutants which one would expect from a clean combusting ICE with the possible exceptions of increased aldehydes, oxygenates, and oxidized sulfur compounds due to their lean (excess oxygen) combustion characteristics. These systems have been poorly characterized, however. Stratified charge engines using heavier fuels (diesel, distillate, etc.), while equally poorly characterized, would be expected to emit higher levels of sulfur compounds, trace metals, particulates, PNA's, and organic particulates than would be expected from the gasoline-fueled stratified charge engine due to the less well refined characteristics of the fuel.

Diesel and rotary engines are used in small numbers in the current light-duty fleet. The current rotary has, before exhaust after-treatment, much higher HC and CO emissions than the ICE. Current rotaries emit higher PNA's, organics, and trace metals than current ICE's due to higher oil consumption. Future rotaries may well solve this problem, which is necessary for increased fuel economy also. Rotary engine emissions, in general, are not significantly different than those from the basic ICE when one excludes the oil combustion effects. The diesel, quite apart from the spark-ignition ICE, is a compression-ignition engine which burns a much less highly refined fuel than gasoline. As a result, non-regulated pollutants are quite different than those from an ICE. High particulate (mostly carbon), odor, SO_2, PNA's, organic particulate, and aldehydes are known. Sulfate emissions are higher than from the ICE due to a 10-fold higher sulfur level in the fuel (the percent of S converted to SO_4 is the same, however, approximately 1%). Diesels have *not* been well characterized but such work is currently under way by EPA. If major use of diesels is considered, pollutants quite different than those from ICE's may be considered for control (particulates, aldehydes, odor).

Sterling, *Rankine*, and *turbine* engines, while only in the early stages of development, are continuous combustion devices quite apart from the intermittent combustion devices discussed above. As a result, HC and CO emissions can be quite low. Non-regulated pollutants have *not* been characterized. However, one would expect changes in emission products associated with the fuel composition such as SO_2, sulfates, PNA's, particulate, organic particulate, and trace metals if heavier fuels were used. High nickel emissions (a carcinogen) have been reported from one developmental turbine.

DISCUSSION

While the current ICE is reasonably well characterized, we are only now gaining the analytical capability to more fully examine detailed non-regulated emissions of potential public health concern. This is particularly true in the general areas of sulfur and nitrogen compounds. The identification of a "new," toxic emission product resulting from the use of a new fuel additive, emission control device, or alternate engine would permit a fairly straight-forward appraisal of potential public health risk. Unfortunately, this is rarely, if ever, the real-world situation. Emissions from mobile sources are immensely complex, contain hundreds of compounds, and are affected by many parameters. PNA's offer an example. PNA emissions increase with increased fuel aromatics, yet the application of oxidation catalyst technology to achieve reduced regulated emissions has resulted in a dramatic related decrease in PNA emissions even when using lead-free higher aromatic content fuels. If we are concerned about the public health consequences of PNA exposures, as we indeed are, the result is a net benefit even though catalyst-equipped vehicles emit higher levels of PNA's with a higher aromatic fuel than would be the case with a lower aromatic fuel.

Sulfuric acid from catalyst-equipped vehicles poses a similar dilemma. Catalyst technology results in decreased human exposures to CO and oxidants. Yet, while the potential exposure to sulfates from all the sulfur in gasoline is only about 1% of the national ambient air burden, the high traffic density localized exposure to directly emitted sulfates from catalyst may well exceed the general ambient levels by several fold. Thus, we must, in the future, be concerned not only with area-wide exposures to automotive-generated pollutants but also to the localized exposures on and near major concentrations of vehicles.

The EPA currently has a number of programs under way to permit such localized and area exposure assessments in the future. In addition, we have undertaken major programs to develop and expand our capability to measure both regulated and non-regulated emissions and to ascertain the impact of fuels, fuel additives, emission control devices, and alternate power systems on such emissions. These studies will be focusing not only upon the details of emission products from the ideally operating systems, but on the effects of non-design operation, such as may occur in the hands of the consuming public, on these emissions. At the present time, however, the qualitative comparisons presented in Table 1 are the best that can be put forth, with the essential understanding that the bulk of our knowledge is associated only with systems 1A and 1B and is essentially void for the other systems considered.

TABLE I

[illegible]

[illegible]

Engine/System	Current Status	[illegible]
1. ICE (Otto Cycle) A. pre-1975	Principal current engine	[illegible]
B. Oxidation Catalyst	~85% of 1975 vehicles so equipped	[illegible]
C. Dual Catalyst	under development	[illegible]
D. 3-Way Catalyst	under development	[illegible]
E. Thermal Reactor	[illegible]	[illegible]
F. Lean Burn	Possible in the near future — under development	[illegible]
G. Stratified Charge	[illegible] development [illegible]	[illegible]
2. Diesel	current medium and heavy duty [illegible] light duty under development	[illegible]
3. Rotary	currently used, small number [illegible]	[illegible]
4. Stirling	long range possibility	[illegible]
5. Rankine	long range possibility	[illegible]
6. Turbine	long range possibility	[illegible]

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TABLE [illegible]

Non-Regulated Pollutants of Public Health Concern

Brief Evaluation of Background

Compound	Toxicological Concern
Pt (Platinum)	Sensitization of platinum [illegible] workers. Body does absorb and distribute [illegible] and [illegible] soluble and [illegible] compounds. [illegible] Toxic at high concentrations. TLV [illegible] (soluble form, as Pt).
[illegible]	Is toxic at high concentrations. May act as [illegible] irritant. Not believed an allergen or respiratory irritant [illegible]. Little data available. No TLV
Ni (Nickel)	[illegible] TLV [illegible] $\mu g/m^3$ as metal, [illegible] $\mu g/m^3$ as soluble salt. Possible [illegible] effects
[illegible]	No data available. No TLV
[illegible][1] [illegible]	Most [illegible] from TLV. Several known to be carcinogenic
[illegible][1]	Several are present. In general, this class of materials is toxic. Irritates the eyes, nose, and throat and [illegible] chronic poisoning [illegible]
Aldehydes[1]/Oxygenates	Reactive organic materials. Many are present in auto exhaust. Generally primary irritation to skin, eyes, and respiratory tract.
Trace Metals	Over 20 [illegible]. Usually [illegible] low concentrations. Some, such as nickel, are carcinogenic. Others, such as iron oxide, appear to act as [illegible]
[illegible]	Toxic to humans. EPA has published [illegible] regulations. TLV 150 $\mu g/m^3$ [illegible]
H_2SO_4 (Sulfuric Acid)	Respiratory irritant. One of the most irritating of the sulfate compounds. Limited human clinical studies. TLV 1000 $\mu g/m^3$
H_2S (Hydrogen Sulfide)	At low concentrations, [illegible] respiratory irritant. At high concentrations (over 600 ppm) lethal systemic poison. TLV 10 ppm ([illegible] $\mu g/m^3$)
COS (Carbonyl Sulfide)	[illegible] toxic gas. [illegible] One case reported lethality at [illegible] ppm after about an hour exposure. No TLV. [illegible]
CS_2 (Carbon Disulfide)	Toxic vapor which affects the central nervous system. Chronic effects reported. TLV 20 ppm ([illegible] $\mu g/m^3$) [illegible] Cardiovascular and neurological effects have been noted from chronic exposure approaching 10 ppm
HCN (Hydrogen Cyanide)	Lethal gas. Immediately fatal at 270 ppm. Principally an acute poison. There are a few reports of chronic [illegible] TLV 10 ppm ([illegible] $\mu g/m^3$)
NH_3 (Ammonia)	Gas irritating to eyes and respiratory system. Reports of temporary blindness and intolerable irritation at high concentrations. TLV 25 ppm ([illegible] $\mu g/m^3$)

[1] See Table 8 for identified emission products.

Reference: TLV's - Threshold Limit Values for Chemical Substances in Workroom Air Adopted by the American Conference of Government Industrial Hygienists for [illegible]. Journal of Occupational Medicine, Vol. [illegible], No. [illegible], January [illegible]

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Identified Phenol, PNA, and Aldehyde Compounds in Automotive Exhausts

PHENOLS

Phenol
O-Cresol
m-Cresol
2,4-Dimethylphenol
2,3-Dimethylphenol
3,4-Dimethylphenol
2,3,5-Trimethylphenol

POLYNUCLEAR AROMATIC HYDROCARBONS

2

Naphthalene

3

Acenaphthylene
Anthracene, A
Alkyl As
Phenanthrene
Trimethylphenanthrenes

4

Benz(a)anthracene, BaA*
Methyl BaA
Chrysene, C*
Methyl C
Dimethyl C
Fluoranthene, Ft
Methyl Ft
Pyrene P
Methyl P
11 H-Benzo(b)fluorene, BbF
Methyl BbF
Triphenylene
Naphthacene

5

Benzo(a)pyrene, BaP*
Methyl BaP
Dimethyl BaP
Benzo(e)pyrene, BeP*
Methyl BeP
Dimethyl BeP
Benzo(ghi)fluoranthene
Benzo(b)fluoranthene*
Benzo(j)fluoranthene*
Benzo(k)fluoranthene*
Dibenz(a,h)anthracene*
Dibenzofluorenes
Perylene

6

Anthanthrene*
Benzo(ghi)perylene
Dibenzo(a,l)naphthacene
Dibenzo(a,e)pyrene*
Dibenzo(a,h)pyrene*
Dibenzo(a,i)pyrene*
Indeno(1,2,3-cd)fluoranthene
Indeno(1,2,3-cd)pyrene*

7

Coronene
Dibenzo(b,pqr)perylene

8

Tribenzo(h,rst)pentaphene

ALDEHYDES

Acetaldehyde
Acrolein + propylene oxide
Propionaldehyde
Methacrolein + methylfuran
Crotonaldehyde
Tiglaldehyde
Benzaldehyde
Tolualdehyde
Ethylbenzaldehyde
Salicylaldehyde

*Carcinogenic

TEST REPORT
AUTOMOTIVE SULFURIC ACID
BASELINE PROGRAM

ENVIRONMENTAL PROTECTION AGENCY
EMISSION CONTROL TECHNOLOGY DIVISION

JANUARY, 1976

SUMMARY

This program involved the testing of 75 vehicles for sulfuric acid and gaseous emissions (HC, CO, NO_x and CO_2). A variety of catalyst and non-catalyst cars were tested. Of the 75 vehicles originally scheduled, 58 have been tested to date. These cars included both current production cars and cars designed to meet advanced emissions standards. The catalyst cars were preconditioned with 500-1,000 miles of modified AMA preconditioning on 0.03% sulfur fuel. The non-catalyst vehicles were tested without preconditioning. Four different labs (EPA-OMSAPC, EPA-ORD, Exxon Research and Engineering Co., and Southwest Research Institute) participated in this program.

The following test schedule was run twice with each car:

FTP
SET
SET
FTP
SET
SET

The average sulfuric acid emissions found over the SET is listed below for different categories of vehicles.

Catalyst vehicles with air injection	about 30 mgpm (range 0.1-96)
Catalyst vehicles without air injection	about 8 mgpm (range 0.5-83)
3-way catalyst vehicles	about 1 mgpm
Non-catalyst vehicles	about 1 mgpm

Two conclusions that can be made from this program are:

(1) There is no definite trend indicating that sulfuric acid emissions increase with the severity of the HC, CO, and NO_x standards. There were vehicles with low sulfuric acid emissions in each category. For example some catalyst vehicles meeting HC, CO, and NO_x standards of .41, 3.4, and 2.0 (or less) gpm had very low sulfuric acid emissions. While some catalyst vehicles in this low emissions category had high sulfuric acid emissions, many catalyst vehicles meeting the more lenient standards of 1.5, 15, and 3.1 gpm HC, CO, and NO_x had equally high sulfuric acid emissions.

(2) The main factor causing high sulfuric acid emissions for cars with either pelleted or monolith catalyst is excess air (oxygen) in the catalyst. This excess oxygen level is frequently independent of whether or not the car has an air pump. For example, a non-air pump catalyst car with a lean calibration could have a high exhaust oxygen level. Some catalyst cars with air pumps may have low sulfuric acid emissions while some catalyst cars without air pumps may have high sulfuric acid emissions.

BACKGROUND:

Work done for the Environmental Protection Agency in 1972 showed much greater emissions of sulfuric acid from catalyst equipped vehicles compared to non-catalyst equipped vehicles. EPA is concerned that sulfuric acid emissions from catalyst equipped vehicles may cause high localized ambient levels of sulfuric acid in congested traffic situations and thus have adverse health effects. To prevent such a problem from occurring, EPA plans to propose automotive sulfuric acid regulations effective for the 1979 model year.

In developing these regulations, EPA devised a new driving cycle (the Sulfuric Acid Emission Test or SET) representative of congested freeway operation where the highest localized sulfuric acid levels are expected to occur. It was necessary to develop a new driving cycle since neither the Federal Test Procedure (FTP)nor the Fuel Economy Test (FET) represent the congested freeway type driving situation.

This cycle was tested extensively in the summer of 1975 in the Test Procedure Development Program. The following four pairs of matched cars supplied by the automobile companies were used.

2 Fords - monolith catalyst with air injection

2 Plymouths - monolith catalyst without air injection

2 Chevrolets - pelleted catalyst without air injection

2 AMC Hornets - pelleted catalyst with air injection

All of the cars except the Fords were designed to meet standards of 1.5, 15, and 3.1 gpm HC, CO, and NO_x respectively over the FTP. The Fords were designed to meet standards of 0.9, 9.0, and 2.0 gpm.

The Test Procedure Development Program involved the testing of the cars on the following sequence with 0.03% sulfur fuel.

1) Run AMA to 6,000 miles
   (regular AMA, 11 laps, 70 mph maximum speed)

2) SEQUENCE A
   Ann Arbor road route - 1 hour
   3 LA 4 (hot start)
   6 hot start emission tests (SET)*
   Ann Arbor road route - 1 hour
   Overnight soak
   Federal test procedure (FTP)*
   Fuel Economy Test (FET)*

Repeat 2) twice for a total of 3 sequences

3) Run 300 miles of modified AMA **

4) SEQUENCE B
   Ann Arbor road route - 1 hour

1 LA-4 (hot start)
Overnight soak
FTP*
SET-2 times*
FET*

Repeat 4) twice for a total of three sequences

5) Repeat 3)

SEQUENCE C

6) Ann Arbor road route - 1 hour
1 LA-4 (hot start)
Overnight soak
FTP*
FET*
SET-2 times*

Repeat 6) twice for a total of three sequences

7) Run SET as many times as necessary until a stable sulfuric acid emission value is obtained.

8) Repeat 3)

* HC, CO, NO_x, Sulfate, and SO_2 Measurement Taken.
** 55 mph top speed, no wide open throttle accelerations.

In addition, Sequence A was run again with modified AMA preconditioning for the cars tested by EPA-OMSAPC and EPA-ORD.

The sulfuric acid emissions from the vehicles without air injection were low, about 1 mgpm. The vehicles with air injection had much higher sulfuric acid emissions, generally from 10 to 70 mgpm.

A summary of the mean values, standard deviations and coefficients of variation for various test cycles are given in Tables 1, 2, 3, 4, and 5.

Table 1 Sulfuric Acid Emissions over the FTP

Table 2 Sulfuric Acid Emissions over the FET

Table 3 Sulfuric Acid Emissions over the SET in Sequence A (SET preceded by Ann Arbor Road Route)

Table 4 Sulfuric Acid Emissions over the SETs in Sequence B (The SET preceded by FTP)

Table 5 Sulfuric Acid Emissions over the SETs in Sequence C (SET preceded by FET)

These values show that the sulfuric acid values for the SET in sequence A are more variable than those in either sequence B or C. This greater variability is probably caused by lack of a specific preconditioning since the Ann Arbor road route involves actual driving in city traffic which is not as reproducible from run to run as dynamometer cycles. The one LA-4 cycle for preconditioning is apparently insufficient to assure reproducible results.

The values in sequence B and C are essentially similar and somewhat more reproducible than those in sequence A. These numbers suggest that it does not seem to make any difference whether the sulfuric acid cycle is preceded by either an FTP or an FET and should give similar emissions when preceded by either cycle. This finding is encouraging since it allows EPA to place the sulfuric acid cycle after either cycle in the certification process.

Another finding from the data is that sulfuric acid emissions are similar for cars preconditioned with either the regular or modified AMA. No statistically significant difference could be found between the two preconditionings.

However, the variability of the sulfuric acid data is high and greater than that found by EPA for gaseous emissions over the FTP. Previous EPA work (SAE Paper 741035) found the following coefficients of variation for gaseous emissions over repetitive FTPs on a catalyst car:

HC	10%
CO	15%
NO_x	7%
CO_2	4%

Coefficients of variation for sulfuric acid emissions are approximately 30-40%. This high variability may mask the differences between the various preconditionings discussed above. The reasons for the higher variability are not known. It was thought that input emissions (HC, CO, NO_x, SO_2, O_2, etc.) to the catalyst were not stable. Tests were run by Exxon, Southwest, and EPA-ORD in which continuous traces of HC, CO, NO_x, CO_2, and sometimes O_2 were taken upstream of the catalyst. These emissions were found to be stable from one cycle to another. Limited tests were run by EPA-[illegible] in which SO_2 was measured continuously downstream of the catalyst. These tests were done with an experimental second derivative spectrophotometer which is just in the process of being applied to automotive exhaust. The readings on this instrument are to be considered only preliminary until more evaluation work is done. However, these readings showed that the instantaneous SO_2 emissions were not as reproducible as were the other gaseous emissions. This work suggests that sulfuric acid storage and release on the catalyst may cause the higher variability.

Following this program, the Baseline Program was started. The main purposes of the Baseline Program were as follows:

(1) to obtain sulfuric acid emission factors on a greater number of currently produced catalyst and non-catalyst vehicles.

(2) to obtain sulfuric acid emission factors on a number of advanced prototype vehicles designed for more stringent control of HC, CO, and NO_x emissions.

VEHICLES

A total of 75 vehicles were scheduled for baseline testing representing a variety of current and advanced emission control systems. The following general categories of vehicles were selected:

(I) Current non-catalyst vehicles

(II) Current catalyst vehicles designed for the following combination of standards:

HC gpm	CO gpm	NO_x gpm
1.5	15	3.1
1.5	15	2.0
.9	9.0	2.0
.4	9.0	1.5
.4	3.4	2.0

(III) Advanced non-catalyst vehicles (stratified charge, lean burn, diesel, lean reactor, rotary engine.)

(IV) Advanced catalyst vehicles (3-way catalyst, start catalyst, modulated air injection, sulfate trap).

(V) Fleet vehicles
3 sets of 5 identical cars to be used to determine car-to-car variability.

A complete listing of the 75 vehicles scheduled for this program and the tests conducted are listed in Table 6. The following four laboratories participated in this program.

AA= EPA-OMSAPC, Ann Arbor, Michigan
RTP= EPA-ORD, Research Triangle Park, North Carolina
SwRI= Southwest Research Institute, San Antonio, Texas
Exxon= Exxon Research and Engineering Co, Linden, N.J.

Of the 75 cars, only 56 have been tested as of this date. Many of the remaining cars will be tested later. Many of the vehicles were supplied by General Motors, Ford, Chrysler, American Motors, and Volvo. These cars included the prototypes designed to meet future standards as well as some production cars meeting the 1975 standards. The rest of the cars were either privately owned or rental vehicles.

TEST SCHEDULE

The catalyst cars were preconditioned using the AMA schedule specified in the Federal Register* except that the wide open throttle acceleration was eliminated and the maximum speed in the last lap was 55 mph. Pelleted and monolith catalyst cars were preconditioned for 1,000 and 500 miles respectively with 0.03% sulfur fuel. A limited number of the GM cars were also preconditioned with the regular AMA (with the wide open throttle acceleration and 70 mph maximum speed included). Preconditioning a limited number of the GM cars with both regular and modified AMA will give a comparison of how the two preconditionings affect sulfuric acid emissions. Each of the laboratories participating in this program did the vehicle preconditioning themselves with either on road or dynamometer operation. However, GM and Ford accumulated AMA mileage on the prototype vehicles supplied to EPA-OMSAPC making additional mileage accumulation on these vehicles unnecessary.

The vehicles were tested in a two day sequence that included sulfuric acid cycles in addition to FTPs and FETs. The exact test sequence is listed below:

23 minute LA-4 preconditioning

Day 1

FTP
SET
SET
FET
SET
SET

Day 2

FTP
SET
SET
FET
SET
SET

Particulate mass, sulfuric acid, HC, CO, NO_x, and frequently SO_2 were measured over all FTPs, SETs, and FETs.

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*Federal Register, Volume 37, No. 221 Part II Page 24319, November 15, 1972

Running the sulfuric acid cycle after both the FTP and FET will give EPA more information on how these two cycles affect emissions over the sulfuric acid cycle. Strictly speaking, additional AMA mileage would have ideally been run before the FET. However, limited data from the Test Procedure Development Program suggest that no trend is apparent on sulfuric acid emission tests which are 1) preceded by AMA mileage accumulation and either an FTP or FET, or, 2) preceded by just an FTP or FET. Also, it would have been impossible to complete the program in the time required if additional AMA mileage accumulation were necessary.

Running two SETs after the FTP and FET gives an indication of how closely a second SET agrees with the first SET. It is possible that the second SET which is preceded by the first SET will be different from the first SET which is preceded by an FTP or FET. Finally, running the entire test sequence a second day will give an indication on the repeatability of the sequence.

RESULTS

A summary of the test results is given in Table 7. This Table lists the following:

(1) the vehicles tested,
(2) the FTP gaseous emissions,
(3) the fuel economy over the FTP and FET,
(4) the average sulfuric acid emissions over the two FTPs,
(5) the average sulfuric acid emissions over the two FETs,
(6) the average, maximum, minimum, standard deviation, and coefficient of variation for the sulfuric acid values over the eight SETs.

The appendix includes a list of all gaseous and sulfuric acid emission values for every test on each of the cars.

The first category (I) of cars tested was current non-catalyst cars including three vehicles with air pumps and one vehicle without an air pump. The three air pump cars were 1975 production cars meeting standards of 1.5, 15, and 3.1 gpm HC, CO, and NO_x. The non-air pump car was a 1972 Chevrolet. Sulfuric acid emissions were very low from all cars, generally less than 1 mgpm. This low level is expected from conventional non-catalyst vehicles.

The next category (II A) of the cars tested was 1975-76 catalyst cars designed to meet standards of 1.5, 15, and 3.1 gpm, HC, CO, and NO_x. Three of the vehicles did not have air injection and had average sulfuric acid emissions under 10 mgpm. Two of these cars were 1975 Plymouths supplied by Chrysler Corporation and tested by Exxon. These cars had sulfuric acid emission rates of 1 mgpm when tested last summer but 7-9 mgpm when tested in the baseline program. The glass fiber filters used by Exxon have a high sulfur background which may affect the accuracy of the results, especially at lower sulfuric acid emission levels such as 1 mgpm. Eight cars were tested with air injection. Seven of these cars showed sulfuric acid emissions of 8-34 mgpm over the SET. These levels are typical for air injection cars. However, the eighth car was a 1975 Granada tested by EPA-ORD. EPA-ORD reports that this car was a "full pass" system with all of the exhaust passing through an Englehard catalyst. The sulfuric acid emissions were extremely low at less than 1 mgpm over the SET. It is not known why the sulfuric acid emissions are this low.

The third category (II B) of cars was catalyst cars designed to meet the 1975 California Standards of 0.9, 9.0, and 2.0 gpm HC, CO, and NO_x. Of the nine cars originally scheduled in this group, four could not be tested this time and will be tested at a later date. Three of the five cars tested had air injection and showed sulfuric acid emissions of 15-30 mgpm over the SET. The two cars without air injection (an Oldsmobile and Buick) showed sulfuric acid emissions over the SET of about 20 mgpm for the Oldsmobile and 6 mgpm for the Buick. The 20 mgpm level is higher than normally expected for non-air pump cars and is probably due to the lean calibration (about 5% exhaust oxygen at idle) The sulfuric acid emission levels of cars in this category are about what would be expected.

The next category (II C) of cars was advanced catalyst prototypes designed to meet 0.4, 3.4, and 2.0 gpm HC, CO, and NO_x. Three of these cars had no air injection. One of these cars was a Volvo prototype and had very low sulfuric acid emissions of 1 mgpm. Two of the other cars were prototype Oldsmobiles with pelleted catalysts but no air pumps. These cars were calibrated somewhat lean (4% oxygen at idle) resulting in higher sulfuric acid than usually expected for non-air pump cars. One of the two cars had average sulfuric acid emissions of 30 mgpm over the SET. The other car had average sulfuric acid emissions of 110 mgpm over the SET. The reasons for the unusually high sulfuric acid emissions from this car are being investigated.

The next category (II D) of cars was catalyst prototypes designed to meet 0.4, 9.0 and 1.5 gpm HC, CO, and NO_x. The one pelleted catalyst vehicle with air injection, an AMC Gremlin, had low sulfuric acid emissions about 5 mgpm over the SET. This vehicle was tested twice to be sure stable sulfuric acid emissions were obtained. The Oldsmobile pelleted catalyst vehicle without air injection had low sulfuric acid emissions of 3 mgpm over the SET. The monolith catalyst vehicle with air injection had sulfuric acid emissions of 24 mgpm over the SET.

The next category (II E) of vehicles was catalyst vehicles designed to meet standards of 1.5, 15 and 2.0 gpm HC, CO, and NO_x. Three of the four non-air injection cars had low sulfuric acid emissions. The fourth non-air pump vehicle (a Chrysler car) had somewhat higher sulfuric acid emissions than expected (about 20 mgpm over the SET) for a non-air pump vehicle. The two air injection vehicles had much higher sulfuric acid emissions. One of these cars emitted 61 mgpm over the SET which is higher than expected.

The next category (III) of vehicles includes advanced non-catalyst concepts such as stratified charge, lean burn, diesel, and rotary engine. The stratified charge, two lean burn, and rotary vehicles all had low sulfuric acid emissions (about 1 mgpm). The Ethyl lean reactor vehicle showed higher sulfuric acid emissions of about 6 mgpm over the SET. There is reason to think that the chloranilate analysis method used for sulfuric acid analysis may give erroneous results when lead salts are present from use of leaded gasoline. Since leaded gasoline had been used with this vehicle immediately before the EPA tests, this vehicle will be retested. The two diesels tested showed high sulfuric acid emissions (about 10-30 mgpm over the SET). The high sulfuric acid emissions are probably caused to a large extent by the higher sulfur content of diesel fuel (0.21%) versus gasoline (0.03%).

The next category (IV) of cars was advanced catalyst prototypes including 3-way catalysts, dual catalysts, and other systems. The three 3-way catalyst vehicles tested had very low sulfuric acid emissions of about 1 mgpm due to the low oxygen level in the exhaust (1% or less). A vehicle with a 3-way catalyst followed by an oxidation catalyst with air injection was tested and had 82 mgpm over the SET. Presumably the higher sulfuric acid emissions are caused by high oxygen levels resulting from air injection. The dual catalyst vehicle containing a Gould reduction catalyst followed by a pelleted oxidation catalyst with air injection had sulfuric acid emissions of 36 mgpm over the SET. A lean burn prototype with air injection and an oxidation catalyst emitted 80 mgpm sulfuric acid the SET. A vehicle with a small start catalyst in front of the oxidation catalyst emitted 40 mgpm sulfuric acid over the SET. A vehicle with a sulfuric acid trap was found to reduce sulfuric acid emissions by 90%. Some of the prototype vehicles scheduled in this category were not available but will be tested as soon as possible.

The final category (V) of vehicles included two sets of five identical cars which would be tested to investigate car to car variability. Five Ford Mavericks were tested in this program and were found to have average sulfuric acid emissions of 35 to 43 mgpm over the SET. The other five vehicles will be tested when they are available.

CONCLUSIONS

This program involved sulfuric acid emission tests of 58 of the 75 vehicles originally scheduled. Emission factors for different catalyst and non-catalyst systems were measured. These tests gave the average emission factors over the SET for air injection and non-air injection catalyst cars as listed below:

Vehicle	Sulfuric Acid
Catalyst vehicles with air injection	about 40 mgpm
Catalyst vehicles without air injection	about 8 mgpm
3-way catalyst vehicles	about 1 mgpm
Non-catalyst vehicles	about 1 mgpm

Two conclusions that can be made from this program are:

(1) There is no definite trend indicating that sulfuric acid emissions increase with the severity of the HC, CO, and NOx standards. There were vehicles with low sulfuric acid emissions in each category. For example, some catalyst vehicles meeting HC, CO, and NO_x standards of .41, 3.4, and 2.0 (or less) gpm had very low sulfuric acid emissions. While some catalyst vehicles in this low emissions category had high sulfuric acid emissions, many catalyst vehicles meeting the more lenient standards of 1.5, 15, and 3.1 gpm HC, CO, and NO_x had equally high sulfuric acid emissions.

(2) The main factor causing high sulfuric acid emissions for cars with either pelleted or monolith catalyst is excess air (oxygen) in the catalyst. This excess oxygen level is frequently independent of whether or not the car has an air pump. For example, a non-air pump catalyst car with a lean calibration could have a high exhaust oxygen level. Some catalyst cars with air pumps may have low sulfuric acid emissions while some catalyst cars without air pumps may have high sulfuric acid emissions.

[illegible]

[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
		[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
			[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
		[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
			[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-

[illegible]

[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	Mean	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
	[illegible]	[illegible]	Std. Dev.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
			Cf. Var.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
[illegible]	[illegible]	[illegible]	Mean	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	Std. Dev.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			Cf. Var.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	Mean	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
	[illegible]	[illegible]	Std. Dev.	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
			Cf. Var.	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
[illegible]	[illegible]	[illegible]	Mean	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
	[illegible]	[illegible]	Std. Dev.	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
			Cf. Var.	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-

[illegible]

[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	Mean	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
	[illegible]	[illegible]	Std. Dev.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
[illegible]	[illegible]	[illegible]	Mean	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	Std. Dev.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	Mean	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
		[illegible]	Std. Dev.	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
			[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
[illegible]	[illegible]	[illegible]	Mean	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
			Std. Dev.	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
			[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-

Table 4: [illegible]
[illegible]

Lab	Vehicle	Catalyst		HC g/mile	CO g/mile	CO_2 g/mile	NO_x g/mile	SO_4 mg/mile	SO_2 mg/mile	MPG
[illegible]	[illegible]	[illegible]	Mean	[illegible]	1.94	[illegible]	[illegible]	[illegible]	-	25.7
	[illegible]	[illegible]	Std. Dev.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
			Coef. Var.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	1.25
[illegible]	[illegible]	[illegible]	Mean	[illegible]	[illegible]	[illegible]	[illegible]	.47	-	-
	[illegible]	[illegible]	Std. Dev.	[illegible]	[illegible]	[illegible]	.52	[illegible]	-	-
			Coef. Var.	[illegible]	[illegible]	7.37	[illegible]	[illegible]	-	-
[illegible]	[illegible]	[illegible]	Mean	[illegible]	[illegible]	-	[illegible]	.75	[illegible]	-
		[illegible]	Std. Dev.	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
			Coef. Var.	[illegible]	[illegible]	-	55.57	[illegible]	[illegible]	-
[illegible]	[illegible]	[illegible]	Mean	[illegible]	[illegible]	-	[illegible]	[illegible]	-	-
		[illegible]	Std. Dev.	[illegible]	[illegible]	-	[illegible]	[illegible]	-	-
			Coef. Var.	[illegible]	[illegible]	-	[illegible]	[illegible]	-	-

Table 5: [illegible]

Lab	Vehicle	Catalyst		HC g/mile	CO g/mile	CO2 g/mile	NOx g/mile	SO4 mg/mile	SO2 mg/mile	MPG
[illegible]	[illegible]	Monolith w/air	Mean	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
			Std. Dev.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
			Cf. Var.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]
[illegible]	Chevrolet Impala	Pellet w/air	Mean	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			Std. Dev.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			Cf. Var.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	Eng. I & II	Monolith w/air	Mean	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
			Std. Dev.	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
			Cf. Var.	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
[illegible]	[illegible] 5 & 6	Pellet w/air	Mean	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
			Std. Dev.	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-
			Cf. Var.	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-

TABLE 6

EPA BASELINE VEHICLES FOR SULFURIC ACID PROGRAM

Category	Vehicle Description	Test Vehicle	Source	Test Lab
I. Current Non-catalyst Vehicles	1. Non Air Pump	72 Chevrolet	Rent	EPA
	2. Air Pump	75 Granada 351	Rent	SwRI
	3. Air Pump	75 Dodge (318)	Rent	SwRI
	4. Air Pump	75 Valiant	Chrysler	GM
II. Current Catalyst Vehicles A. 1.5,15,3.1 gpm. HC,CO, NOx	1. Pellet w/air	75 Hornet (304)	AMC	SwRI
	2. Pellet no air	75 Chev. (350)	GM	EPA
	3. Pellet no air	75 Malibu (350)	Rent	EPA
	4. Monolith w/air	76 Maverick (302)	Ford	GM
	5. Monolith w/air	75 Maverick	Rent	EPA
	6. Monolith w/air	76 Ford LTD (351)	Ford	GM
	7. Monolith w/air	75 Torino	Rent	EPA
	8. Monolith w/air	75 Torino	Rent	EPA
	9. Monolith w/air	75 Maverick (250)	Rent	EPA
	10. Monolith no air	75 Plymouth	Chrysler	[illegible]
	11. Monolith no air	75 Plymouth	Chrysler	[illegible]
	12. Monolith w/air	75 Granada	Rent	EPA
B. 0.9,9,2.0 (Calif)	1. Pellet w/air	75 Chevrolet (350)	Lease	SwRI
	2. Pellet w/air	75 Mustang (304)	Rent	EPA
	3. Pellet w/air	75 Cadillac (500)	Rent	EPA
	4. Pellet no air	75 Vega (140)	Rent	EPA
	5. Pellet no air	75 Olds. Cutlass (455)	GM	GM
	6. Monolith w/air	Gran Torino (360)	Lease	SwRI
	7. Monolith w/air	Granada (302)	Ford	GM
	8. Monolith no air	Audi 100LS (114) or Audi Fox (97) California	Rent or from Audi	EPA
	9. Pellet no air	75 Buick	GM	GM
C. 0.4,3.4,2.0	1. Pellet w/air	Chevrolet	GM	GM
	2. Pellet w/air	Pontiac	GM	GM
	3. Pellet no air	Olds.	GM	GM
	4. Pellet no air	Olds.	GM	GM
	5. Monolith w/air	77 Mercury	Ford	GM
	6. Monolith w/air		Chrysler	GM
	7. Monolith lean mixture, no air injection	Volvo	Volvo	GM
	8. Monolith w/air	Volvo	Volvo	GM

TABLE [illegible] (cont'd)

[illegible] VEHICLES [illegible]

Category	Vehicle Description	Test Vehicle	Source	Test Lab
I. [illegible]	1. Pellet w/air	[illegible]	[illegible]	[illegible]
	2. Pellet no air	[illegible]	[illegible]	[illegible]
	3. Monolith w/air		Chrysler	[illegible]
II. [illegible]	1. Pellet no air		[illegible]	[illegible]
	2. Pellet		[illegible]	[illegible]
	3. Monolith no air		Chrysler	[illegible]
	4. Monolith no air	[illegible] (1975)	Ford	[illegible]
	5. Monolith w/air	[illegible] (1975) [illegible]	Ford	[illegible]
	6. Pellet w/air	73 Chev. [illegible] (350) [illegible] axle	[illegible]	[illegible]
	7. Pellet no air	73 Chev. [illegible] (350) [illegible] axle	[illegible]	[illegible]
	8. Monolith w/air	73 Ford [illegible] 3.25 axle	[illegible]	[illegible]
	9. Monolith no air	73 Dodge Van (318) 3.55 axle	[illegible]	[illegible]
III. Advanced Non-Catalyst Systems	1. Strat. Charge	[illegible]		[illegible]
	2. Rotary/[illegible]	[illegible]		[illegible]
	3. Lean Burn		Chrysler	[illegible]
	4. Lean Burn		Chrysler	[illegible]
	5. Diesel	[illegible]		[illegible]
	6. Diesel	[illegible]		[illegible]
	7. Lean Reactor	[illegible]	[illegible]	[illegible]
	8. Diesel	VW Rabbit (Diesel)	[illegible]	[illegible]
IV. Advanced Catalyst Concepts [illegible] ([illegible])	1. 3-way Fuel Inject., no air	Volvo	Volvo	[illegible]
	2. 3-way	[illegible]	[illegible]	[illegible]
	3. 3-way		[illegible]	[illegible]
	4. 3-way, Fuel Injection	Pinto	Ford	[illegible]
	5. Lean Burn Oxidation Cat.		[illegible]	[illegible]
	6. Start Cat.		[illegible]	[illegible]
	7. Start Cat.		Chrysler	[illegible]
	8. Dual Catalyst		[illegible]	[illegible]
	9. Red. Air		[illegible]	[illegible]
	10. [illegible] Air		[illegible]	[illegible]
	11. Sulfate Trap		[illegible]	[illegible]
	12. 3-way [illegible] + air inj. [illegible]		Ford	[illegible]

*Many of these cars were designed for NO_x emissions above [illegible] gpm

[illegible]

[illegible]

Category	Vehicle Description	Test Vehicle	Source	Test Lab
[illegible]	1. [illegible]	[illegible]	[illegible]	[illegible]
	2. [illegible]	[illegible]	[illegible]	[illegible]
	3. [illegible]	[illegible]	[illegible]	[illegible]
	4. [illegible]	[illegible]	[illegible]	[illegible]
	5. [illegible]	[illegible]	[illegible]	[illegible]
	6. [illegible]	[illegible]	[illegible]	[illegible]
	7. [illegible]	[illegible]	[illegible]	[illegible]
	8. [illegible]	[illegible]	[illegible]	[illegible]
	9. [illegible]	[illegible]	[illegible]	[illegible]
	10. [illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]	[illegible]	HC	CO	NOx	FTP	SET	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	C.R.
I. Current Non-Catalyst Vehicles													
	1. [illegible] Air Pump	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	2. Air Pump	[illegible]	[illegible]	[illegible]	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	3. Air Pump	[illegible]	[illegible]	[illegible]	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	4. Air Pump	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
II. Current Catalyst Vehicles													
	a. [illegible] gpm HC,CO,NOx												
	1. Pelleted w/air	[illegible]	[illegible]	[illegible]	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	2. Pelleted no air	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	3. Pelleted no air	NOT ANALYZED											
	4. Mono. w/air	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	5. Mono. w/air	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	6. Mono. w/air	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	7. Mono. w/air	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	8. Mono. w/air	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	9. Mono. w/air	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	10. Mono. no air	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	11. Mono. no air	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	12. Mono. w/air	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	b. [illegible] gpm HC, CO, NOx (California)												
	1. Pelleted w/air	[illegible]	[illegible]	[illegible]	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	2. Pelleted w/air	NOT ANALYZED											
	3. Pelleted w/air	NOT ANALYZED											
	4. Pelleted no air	NOT ANALYZED											
	5. a. [illegible] no air ([illegible])	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	b. [illegible] no air ([illegible])	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	6. Mono. w/air	[illegible]	[illegible]	[illegible]	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	7. Mono. w/air	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	8. Mono. no air	NOT ANALYZED											
	9. Pelleted no air	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE [illegible] (Cont'd)

CATEGORY	VEHICLE DESCRIPTION	FTP GASEOUS EMISSIONS (g/mi) HC	CO	NOx	FUEL ECONOMY (mpg) FTP	HFET	FTP [illegible]	HFET [illegible]	[illegible] EMISSIONS (mg/mi) [illegible]	[illegible]	[illegible]	S.D.	C.V.
C. 0.4, 3.4, 2.0 gpm HC, CO, NOx													
	1. Fiat, w/air	0.42	2.39	1.98	31.4	37.4	9.6	46.9	49.6	78.9	48.7	6.9	0.28
	2. a. Fiat, w/air (Rel. [illegible] Traceo.)	0.36	4.39	1.26	31.2	35.8	5.2	73.1	32.1	49.3	34.2	22.4	0.27
	b. Fiat, w/air (Rel. [illegible] Traceo.)	0.29	2.81	1.51	31.7	38.2	1.9	46.3	21.7	42.1	9.3	31.2	0.52
	3. Pelleted no air	0.32	2.33	1.55	30.5	36.3	11.8	138.2	46.2	114.7	74.6	19.2	0.25
	4. Pelleted no air	0.32	0.79	1.40	30.2	35.2	11.6	39.6	29.3	47.[illegible]	[illegible]	36.7	0.41
	5. Mono. w/air	0.25	1.09	1.21	9.6	35.0	7.2	33.1	38.3	37.7	34.1	30.6	0.35
	6. Mono. w/air	0.26	2.96	1.39	22.0	36.4	25.4	76.7	40.5	122.9	51.[illegible]	27.6	0.36
	7. Mono. no air/[illegible]	0.40	4.99	1.25	30.7	35.5	4.3	–	1.6	3.7	2.0	1.8	0.37
	8. Mono. w/air	0.34	1.36	1.64	30.0	33.7	10.7	65.2	30.9	76.0	40.7	38.7	0.39
D. 0.4, 9.0, 1.5 gpm HC, CO, NOx													
	1. Pelleted w/air	0.37	1.47	1.55	29.1	37.2	4.9	9.2	5.2	22.8	1.3	3.2	0.30
	2. Pelleted no air	0.40	4.02	0.99	33.2	38.4	2.1	4.0	2.4	2.6	1.9	0.4	0.28
	3. Mono. w/air	0.40	7.09	1.40	27.0	34.0	2.1	16.0	25.9	31.7	4.2	10.2	0.38
E. 1.5, 15.0, 2.0 gpm HC, CO, NOx													
	1. Pelleted no air	0.39	4.81	1.61	34.1	39.2	2.1	4.7	3.3	6.7	1.2	1.9	0.57
	2. Pelleted no air	0.39	5.02	1.89	34.1	39.6	2.6	3.5	3.7	12.8	1.5	3.5	0.46
	3. Mono. no air	1.37	6.39	1.65	26.5	32.2	3.6	9.5	[illegible]	25.4	19.2	2.5	0.31
	4. Mono. no air	0.39	2.96	1.76	34.9	31.[illegible]	4.9	8.7	2.9	6.4	1.5	1.3	0.47
	5. Mono. w/air	0.40	1.80	1.75	34.4	39.6	4.4	109.3	65.3	106.9	58.6	17.7	0.21
	6. Pelleted w/air	0.40	3.70	3.20	25.5	36.0	9.5	25.8	32.7	25.4	3.2	8.7	0.60
	7. Pelleted no air	NOT AVAILABLE											
	8. Mono. w/air	NOT AVAILABLE											
	9. Mono. no air	NOT AVAILABLE											
III. Advanced Non-Catalyst Systems													
	1. Stratified Charge	0.30	3.05	1.05	25.2	33.4	0.5	12.6	2.0	3.6	0.7	1.0	0.40
	2. Rotary/TRP	2.02	20.34	1.50	20.1	27.1	1.8	2.2	1.5	3.4	0.4	1.1	0.70
	3. Lean Burn	0.37	4.81	2.21	28.3	38.0	0.2	0.3	0.4	0.9	0.3	0.2	0.40
	4. Lean Burn	0.40	4.37	2.33	31.4	38.9	1.8	1.8	1.6	2.0	0.9	0.7	0.46
	5. Diesel	NOT AVAILABLE											
	6. Diesel	–	0.74	1.26	–	–	27.0	23.3	17.4	28.7	20.9	1.2	0.07
	7. Lean Reactor	0.36	6.40	1.88	21.0	28.2	22.8	9.2	6.2	7.7	5.2	1.8	0.26
	8. Diesel	0.72	0.90	1.22	36.5	50.2	8.5	4.0	9.4	18.2	6.6	0.7	0.07

TABLE 7 (cont'd)

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	—	—	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	—	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	—	—	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	—	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
231 [illegible]	0.65	0.71	2.06	90.8	9.7	61.7	4.8	61.7	22.8
232 [illegible]	1.78	0.36	2.67	225.6	18.6	108.1	6.2	59.2	26.7
233 [illegible]	1.78	0.27	2.76	224.1	18.5	95.4	5.9	59.2	26.7
234 [illegible]	1.98	0.32	2.88	238.6	16.8	128.9	9.2	57.8	25.5
235 [illegible]	1.67	0.25	2.79	188.4	9.9	93.8	5.7	58.3	25.9
236 [illegible]	1.82	0.25	2.62	207.3	18.8	104.7	5.9	56.8	25.7
237 [illegible]	0.45	0.19	2.38	91.6	9.8	57.8	3.7	61.3	21.1
238 [illegible]	1.88	0.27	2.69	252.8	22.7	127.6	7.1	59.9	26.5
239 [illegible]	1.5	0.22	3.36	238.2	7.2	131.5	4.1	59.3	26.7
240 [illegible]	1.38	0.26	4.26	267.5	21.5	135.1	9.8	56.7	22.8
241 [illegible]	2.22	0.26	3.35	248.7	5.2	138.8	2.9	59.2	26.7
242 [illegible]	2.5	0.26	3.46	235.6	6.8	131.6	3.3	59.6	26.7
243 [illegible]	1.81	0.22	3.46	237.9	6.7	135.1	3.7	59.9	26.6
244 [illegible]	2.61	0.22	3.51	238.2	6.3	138.3	3.5	59.8	26.7
245 [illegible]	1.86	0.19	3.61	64.6	7.8	56.5	3.9	59.3	26.7

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	—	—	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	2.82	0.31	5.73	69.3	6.9	42.7	3.8	45.2	22.3
[illegible]	"	0.57	0.22	7.71	42.0	5.8	35.8	3.3	58.2	26.7
[illegible]	"	0.50	0.21	7.88	52.3	4.6	45.8	2.6	57.3	25.1
[illegible]	"	0.39	0.21	9.48	65.3	2.9	59.7	1.8	54.7	30.1
[illegible]	"	0.40	0.22	8.45	44.7	3.8	39.3	2.2	57.4	25.8
[illegible]	"	0.39	0.22	7.33	67.9	3.3	48.7	1.8	59.8	24.8
[illegible]	"	1.76	0.29	5.86	35.3	8.2	23.8	3.6	80.3	21.1
[illegible]	"	0.51	0.21	8.25	54.9	5.5	52.8	3.5	52.8	26.3
[illegible]	"	—	—	—	61.9	4.5	55.9	2.6	57.4	25.1
[illegible]	"	0.26	0.27	9.85	46.6	7.2	40.5	4.5	58.6	26.6
[illegible]	"	0.60	0.21	8.31	82.3	5.8	78.9	2.9	57.8	26.9
[illegible]	"	—	—	—	58.6	5.2	45.1	3.1	56.1	25.5
[illegible]	"	0.38	0.22	7.39	84.2	3.8	73.4	2.2	57.6	25.8
[illegible]	"	0.35	0.22	7.03	64.5	5.8	57.1	3.4	55.5	26.9
[illegible]	"	0.86	0.23	6.80	65.2	3.8	56.6	2.7	58.7	26.8

[illegible]

[illegible]

[illegible]

[illegible]

Test No.	Test Date	Test Type	HC	CO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Total Recovery	[illegible]
1	10/7/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1	10/8/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		avg.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
2	10/7/75	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2	10/8/75	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
3	10/7/75	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3	10/8/75	S-7	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	—	—	[illegible]
		avg.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
4	10/7/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4	10/8/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		avg.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
5	10/7/75	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5	10/8/75	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		avg.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
6	10/7/75	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6	10/8/75	S-7	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		avg.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
Avg. of 6 [illegible]			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]				[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]				
[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

			[illegible]							
Date	Test Type	Duration	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Total Recovery
[illegible]	[illegible]			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

1975 California [illegible]

[illegible] Catalyst with Air Pump

([illegible] Sulfur Fuel)

Test No.	Date	Test Type	[illegible] HC	CO	NOx	SO2	mg/km H2SO4	Sulfur as S in H2SO4	Sulfur as S in SO2	Total Recovery
1	10/2/75	FTP	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1	10/3/75	FTP	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		avg.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2	10/2/75	SET-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2	10/3/75	SET-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		avg.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3	10/2/75	SET-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3	10/3/75	SET-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		avg.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4	10/2/75	FET	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4	10/3/75	FET	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		avg.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5	10/2/75	SET-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5	10/3/75	SET-7	[illegible]	[illegible]	[illegible]	[illegible]	—	—	[illegible]	—
		avg.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6	10/2/75	SET-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6	10/3/75	SET-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		avg.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
avg. of 8	SET-7's		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible] Injected [illegible]

[illegible] 3 Way Catalyst, No Air Injection

Date	Test No.	Test Type	Duration	HC	CO	NOx	SO2	mg/km H2SO4	SO4 as % of Fuel S	SO2 as % of Fuel S	Total Recovery
10/28/75	1	FTP		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
10/29/75	1	FTP		[illegible]	[illegible]	[illegible]	[illegible]	—	—	[illegible]	—
				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
10/28/75	2	SET-7	23 min	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
10/29/75	2	SET-7	23 min	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
10/28/75	3	SET-7	23 min	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
10/29/75	3	SET-7	23 min	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
10/28/75	4	FET	12 min	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
10/29/75	4	FET	12 min	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
10/28/75	5	SET-7	23 min	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
10/29/75	5	SET-7	23 min	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
10/28/75	6	SET-7	23 min	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
10/29/75	6	SET-7	23 min	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
				[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

BASELINE EMISSIONS TEST RESULTS
1975 FORD PINTO, BASELINE CAR IT-4 [illegible]
[illegible] 3-WAY CATALYST PLUS OXIDATION CATALYST WITH AIR
(0.10% FUEL SULFUR)

Test	Date	Test Type	g/km HC	g/km CO	g/km NO_x	g/km SO_2	mg/km H_2SO_4	% Fuel S as S in H_2SO_4	% Fuel S as S in SO_2	Total Recovery
1	10/6/75	FTP	0.09	1.35	1.43	0.048	35.10	38.99	82.21	121.20
1	10/7/75	FTP	0.11	1.57	1.37	0.021	13.86	16.99	40.30	57.29
		Avg.	0.10	1.46	1.40	0.034	24.46	27.99	61.26	89.25
2	10/6/75	SET-7	0.01	1.14	1.61	0.067	63.67	96.02	107.96	204.02
2	10/7/75	SET-7	0.01	1.10	1.59	0.059	61.56	97.96	93.98	191.96
		Avg.	0.01	1.12	1.60	0.063	62.63	97.02	100.96	197.98
3	10/6/75	SET-7	0.01	1.11	1.53	0.052	58.66	87.48	73.65	161.05
3	10/7/75	SET-7	0.01	1.19	1.56	0.060	46.56	72.22	95.33	167.55
		Avg.	0.01	1.15	1.54	0.056	52.61	79.85	84.40	164.20
4	10/6/75	FET	0.01	1.00	1.66	0.057	43.58	72.79	91.07	161.86
4	10/7/75	FET	0.01	1.04	1.84	0.015	59.92	96.85	83.35	181.89
		Avg.	0.01	1.02	1.75	0.036	51.76	84.82	87.26	171.67
5	10/6/75	SET-7	0.01	1.09	1.69	0.032	39.55	59.46	74.72	134.18
5	10/7/75	SET-7	0.00	1.03	1.57	——	57.66	91.76	——	——
		Avg.	<0.01	1.06	1.63	0.032	48.61	75.61	74.72	134.18
6	10/6/75	SET-7	0.01	1.01	1.57	0.021	37.20	58.98	51.71	110.68
6	10/7/75	SET-7	0.00	1.11	1.48	0.025	42.52	65.49	58.96	124.40
		Avg.	<0.01	1.06	1.52	0.023	39.86	62.26	55.33	117.56
	Avg. of 8 SET-7's		0.01	1.07	1.57	0.036	51.95	78.67	73.46	150.25

[illegible]
[illegible]
[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

Test No.	Date	Test Type	HC	CO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Total Recovery
1	10/23/75	FTP	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1	11/06/75	FTP	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2	10/23/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2	11/06/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3	10/23/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3	11/06/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4	10/23/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4	11/06/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5	11/06/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6	10/23/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6	11/06/75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible] Data

[illegible]

TABLE 1 (Cont'd)

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]
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	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 3 (cont'd)

Vehicle	Test	HC g/m	CO g/m	NOx g/m	CO2 g/m	Fuel Economy mpg	NH3 mg/m
	SC	.172	1.344	[illegible]	516	17.2	5.1
	SC	.092	1.274	[illegible]	437	20.4	6.1
Honda CV-4	FTP	1.463	13.922	1.4[illegible]	726	22.8	3.6
III A	HWFET	.778	8.442	1.900	565	25.8	7.8
	HWFET	1.188	26.071	1.344	402	20.9	1.3
	SC	17.720	65.654	1.744	349	17.8	3.6
	SC	1.468	26.952	[illegible]	394	17.7	1.7
	SC	1.261	8.659	1.544	616	23.7	8.7
	SC	.532	4.724	1.748	682	23.6	4.8
	SC	11.734	71.823	1.327	423	25.2	3.5
	SC	.679	22.794	1.362	773	21.6	3.2
	SC	14.189	46.774	1.284	338	20.4	2.3
	SC	.806	6.474	1.871	711	22.8	2.2
	SC	8.523	46.679	1.578	636	25.4	1.1
	SC	1.302	4.806	1.3[illegible]	664	23.7	2.4
	SC	6.938	52.492	1.675	635	20.8	1.1
1975 Blue Ford Torino, monolith catalyst with air injection designed for 1.5,15,3.1 gpm HC,CO, NOx. III A 7	FTP	1.154	4.967	2.77[illegible]	784	18.7	5.6
	FET	.703	2.168	2.961	876	18.5	20.8
	FET	.566	2.062	2.044	756	21.5	22.8
	SC	.778	2.459	3.298	722	22.1	22.2
	SC	.572	2.914	3.276	685	22.4	24.4
	LA-4	1.178	3.229	2.098	772	22.1	22.2
	SC	.612	2.313	4.298	690	22.4	18.6
	SC	.422	2.925	2.774	631	23.6	25.2
	SC	.700	4.221	3.225	694	22.6	18.8
	SC	.796	3.779	3.256	660	23.8	18.3
	SC	.785	3.715	4.689	661	23.4	18.6
	SC	.742	4.422	3.292	697	22.3	22.2
	SC	.833	3.772	3.151	689	23.8	23.5
	SC	.678	3.582	2.846	667	22.3	22.9
	SC	.661	4.429	2.986	702	22.2	22.8
	SC	.742	4.139	3.115	697	22.3	23.1
	FTP	1.676	3.802	3.389	800	22.3	22.3
1975 Yellow Ford Torino monolith catalyst with air injection designed for 1.5,?,3.1gpm NOx HC,CO. III A 4	FET	.748	2.998	2.602	584	24.8	30.2

[illegible]

[illegible]	[illegible]	[illegible] g/mi	[illegible] g/mi	[illegible] g/mi	[illegible] g/mi	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 2

Sulfate Test Program Results
Test Sequence

EPA-RTP Data

FTP
SC
SC
FET
FET
SC
SC

The following vehicles were run with a 5,000 CFM cooling fan:

Honda CVCC, Mazda RX-4, 2 [illegible], Chevrolet 350, Blue Impala (Series I)

The following vehicles were run with a larger 22,000 CFM cooling fan:

Granada, Blue Impala (Series 2), 2 Mavericks

All cars were run with 0.03% sulfur fuel except the Granada which ran on 0.03% sulfur fuel containing a manganese fuel additive.

The tests are given in the order run.

Vehicle	Test	HC g/mi	CO g/mi	NOx g/mi	CO2 g/mi	Fuel Economy mpg	SO4 mg/mi
			Series 1 (5,000 CFM fan)				
1975 Blue Chev. Impala (supplied to EPA by GM), oxidation catalyst, no air injection, designed for 1.5, 15, 3.1 gpm HC, CO, NOx. II A2	FTP	.433	10.53	1.729	727	12.7	-
	SC	.369	13.52	1.81	571	15.1	0.8
	SC	.440	15.26	1.22	552	16.2	0.1
	FET	.348	10.36	1.22	527	16.8	0.2
	FET	.427	10.5	1.12	541	16.6	0.2
	SC	1.03	55.30	1.15	521	16.2	0.1
	SC	1.07	57.71	1.20	506	16.5	2.06
	FTP	.365	8.53	1.42	683	12.5	0.1
	SC	.381	9.43	1.16	557	15.8	0.1
	SC	.348	36.23	.960	487	15.9	0.07
	FET	.173	29.70	1.11	477	16.8	0.1
	FET	.256	3.78	1.33	501	15.2	0.3
	SC	.480	38.60	1.83	521	15.3	0.2
	SC	1.01	41.70	1.76	585	15.1	0.8

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

I1

IAQ

TABLE 2 (cont'd)

Vehicle	Test	HC g/m	CO g/m	NOx g/m	CO2 g/m	Fuel Economy mpg	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Honda CVCC III.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1975 Blue Ford Maverick, monolith catalyst with air injection designed for 1.5, 15,3.1 gpm HC,CO,NOx II A 5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 2 (cont'd)

Vehicle	Test	HC g/mi	CO g/mi	NOx g/mi	CO2 g/mi	Fuel Economy mpg	SO4 mg/mi
	SC	.086	.308	1.352	416	20.2	30.3
	FET	.078	0	1.445	425	20.9	40.1
	FET	.287	.322	1.406	427	20.4	30.5
	SC	.086	[illegible]	1.483	403	21.7	43.9
	SC	.080	.345	1.406	402	20.7	45.4
1975 [illegible] Ford [illegible], mono-lith catalyst with air injection designed for 1.5, 15,3.1gpm HC,CO, NOx [illegible]	FTP	.227	.228	1.460	516	15.7	6.9
	SC	.087	.344	1.346	400	17.8	21.9
	SC	.107	0	1.406	409	17.8	27.9
	FET	.155	.073	1.426	401	20.1	27.3
	FET	.136	.101	1.485	449	18.5	23.8
	SC	.125	[illegible]	1.387	446	18.8	18.6
	SC	.107	.305	1.486	432	16.2	22.4
	FTP	.258	.481	1.387	539	16.1	—
	SC	.096	.322	1.501	507	16.8	—
	SC	.095	.175	1.497	457	19.9	—
	FET	.083	.210	1.467	402	19.7	—
	FET	.134	.207	1.460	459	18.9	—
	SC	.083	0	1.228	432	20.1	—
	SC	.086	0	1.366	434	20.1	—
[illegible] ED-4 [illegible]	FTP	1.12	31.46	1.52	546	14.8	1.2
	SC	1.15	12.86	1.63	457	17.6	3.4
	SC	1.67	46.99	1.42	438	16.9	1.8
	FET	.989	26.33	1.33	408	16.6	3.6
	FET	.942	33.56	1.39	467	16.9	1.2
	SC	.457	4.84	1.30	521	16.2	2.6
	SC	10.75	66.31	1.36	376	17.1	8.9
	FTP	1.56	33.89	1.47	672	12.2	2.3
	SC	1.07	16.46	1.12	352	15.8	8.4
	SC	13.06	73.56	1.36	348	17.1	8.4
	FET	9.250	48.10	1.15	304	19.9	1.2
	FET	1.835	7.57	1.40	362	15.1	2.8
1975 [illegible] Ford [illegible], monolith catalyst with air injection designed for 1.5,15,3.1 gpm HC,CO, NOx [illegible]	SC	1.30	25.11	1.42	506	15.6	1.5
	FTP	1.00	5.05	2.56	380	11.2	13.3

TABLE 2 (cont'd)

Vehicle	Test	HC g/mi	CO g/mi	NOx g/mi	CO2 g/mi	Fuel Economy mpg	SO4 mg/mi
1975 [illegible], monolith catalyst with air injection designed for 1.5, 15, 3.1 gpm HC, CO, NOx.	SC	[illegible]	[illegible]	[illegible]	[illegible]	13.4	21.6
	SC	[illegible]	[illegible]	[illegible]	[illegible]	13.6	11.5
	FET	[illegible]	[illegible]	[illegible]	[illegible]	12.7	15.3
	FET	[illegible]	[illegible]	[illegible]	[illegible]	13.6	20.4
	SC	[illegible]	[illegible]	[illegible]	[illegible]	13.0	20.2
	SC	[illegible]	[illegible]	[illegible]	[illegible]	13.5	15.4
	FTP	[illegible]	[illegible]	[illegible]	[illegible]	11.2	7.85
	SC	[illegible]	[illegible]	[illegible]	[illegible]	13.3	23.8
	SC	[illegible]	[illegible]	[illegible]	[illegible]	15.6	17.2
	FET	[illegible]	[illegible]	[illegible]	[illegible]	14.1	17.9
	SC	[illegible]	[illegible]	[illegible]	[illegible]	14.3	12.6
	SC	[illegible]	[illegible]	[illegible]	[illegible]	13.3	4.9
	FTP	1.51	[illegible]	[illegible]	[illegible]	14.4	8.6
	SC	[illegible]	[illegible]	[illegible]	[illegible]	15.3	20.7
	SC	[illegible]	[illegible]	[illegible]	[illegible]	15.6	18.4
	FET	[illegible]	[illegible]	[illegible]	[illegible]	16.0	13.5
	FET	[illegible]	[illegible]	[illegible]	[illegible]	15.1	16.1
	SC	[illegible]	[illegible]	[illegible]	[illegible]	16.1	11.6
	SC	[illegible]	[illegible]	[illegible]	[illegible]	15.6	10.2
	FTP	[illegible]	[illegible]	[illegible]	[illegible]	13.1	7.2
	SC	[illegible]	[illegible]	[illegible]	[illegible]	15.4	18.8
	SC	[illegible]	[illegible]	[illegible]	[illegible]	15.7	24.3
	FET	[illegible]	[illegible]	[illegible]	[illegible]	15.1	24.3
	FET	[illegible]	[illegible]	[illegible]	[illegible]	14.1	20.3
	SC	[illegible]	[illegible]	[illegible]	[illegible]	15.3	20.8
	SC	[illegible]	[illegible]	[illegible]	[illegible]	15.2	22.7

I A3

[illegible]

[illegible]

[illegible]

Run no.	Type	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	2.8%	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	17.7	4.3
[illegible]	5-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	31.2	29.2
[illegible]	5-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	27.8	16.3
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	25.9
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	30.5	27.9
[illegible]	5-7	.272	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	22.7
[illegible]	5-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	25.5
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	25.2	11.4
[illegible]	5-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	15.9	22.5
[illegible]	5-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	15.9	16.5
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	23.2	21.2
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	5-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	21.3	37.2
[illegible]	5-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	16.3

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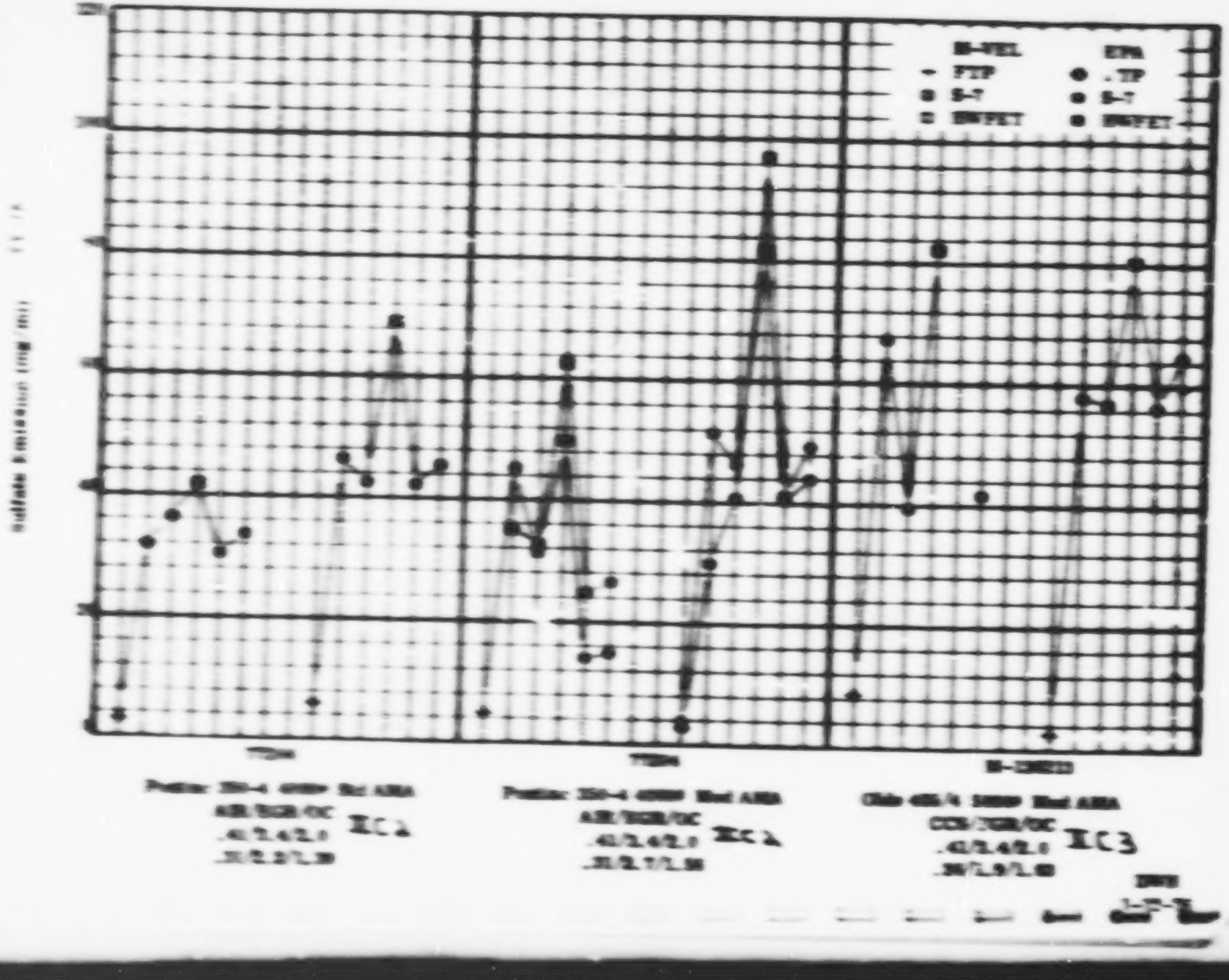
EPA Sulfate Baseline Program



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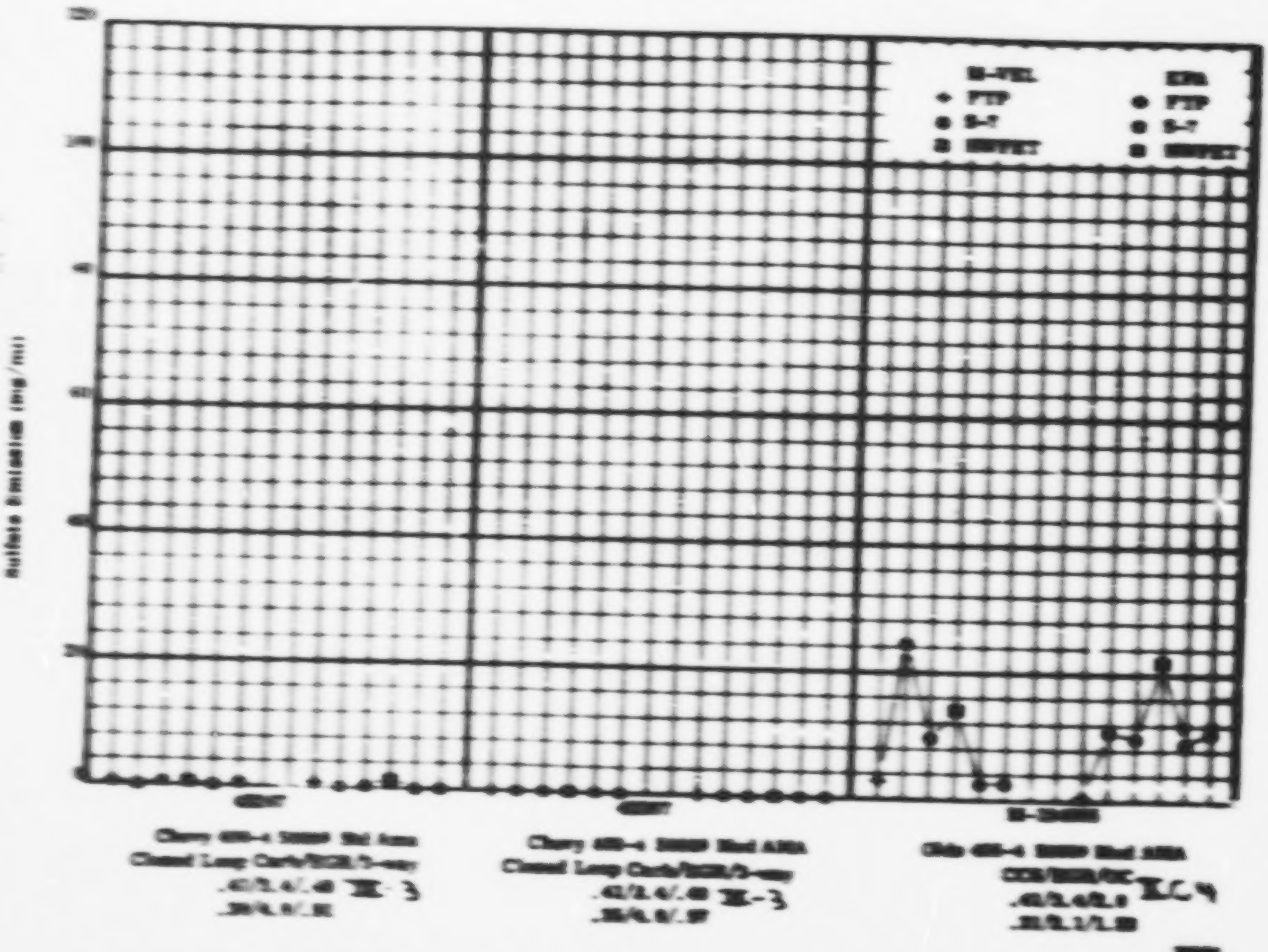

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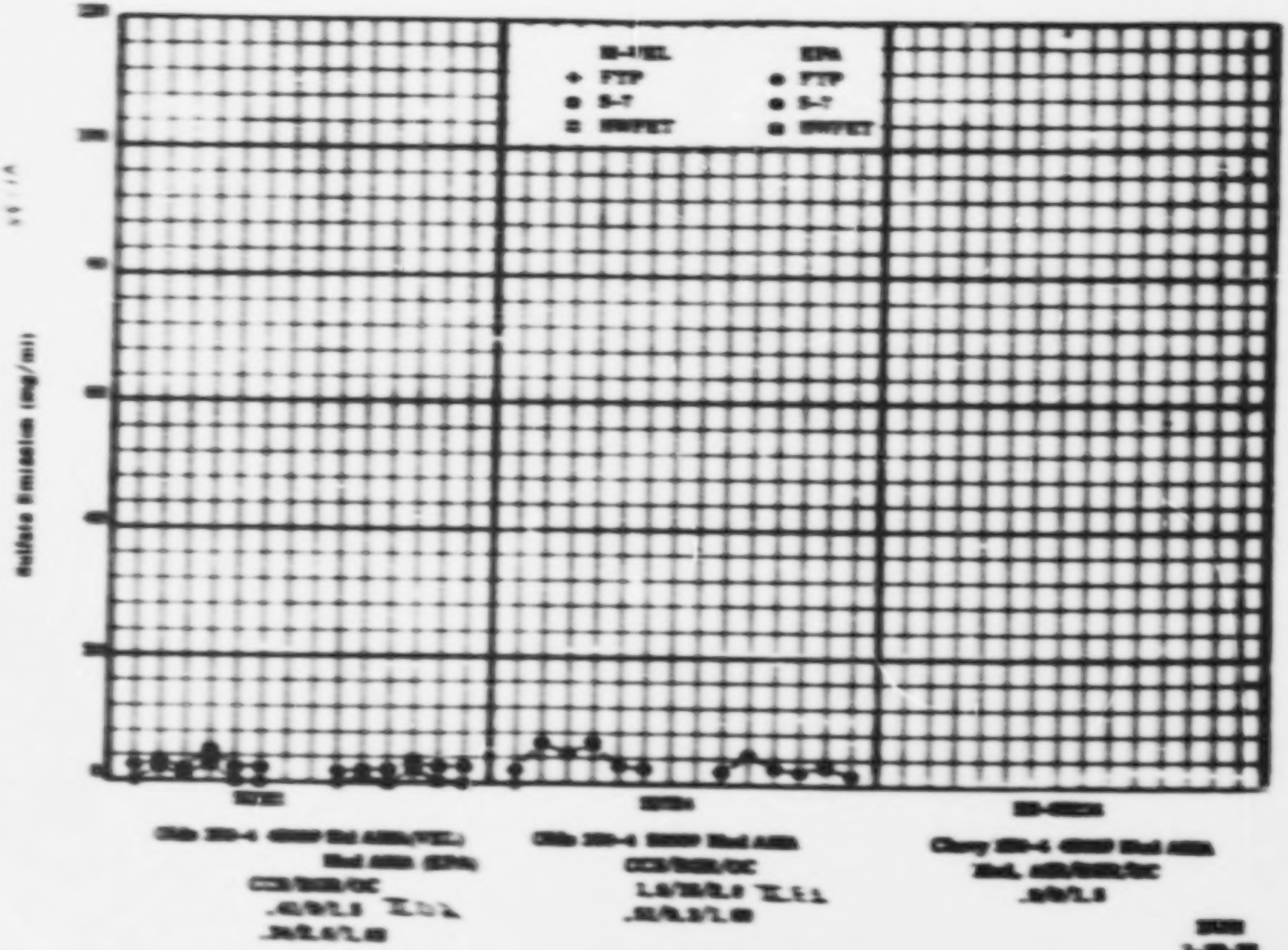

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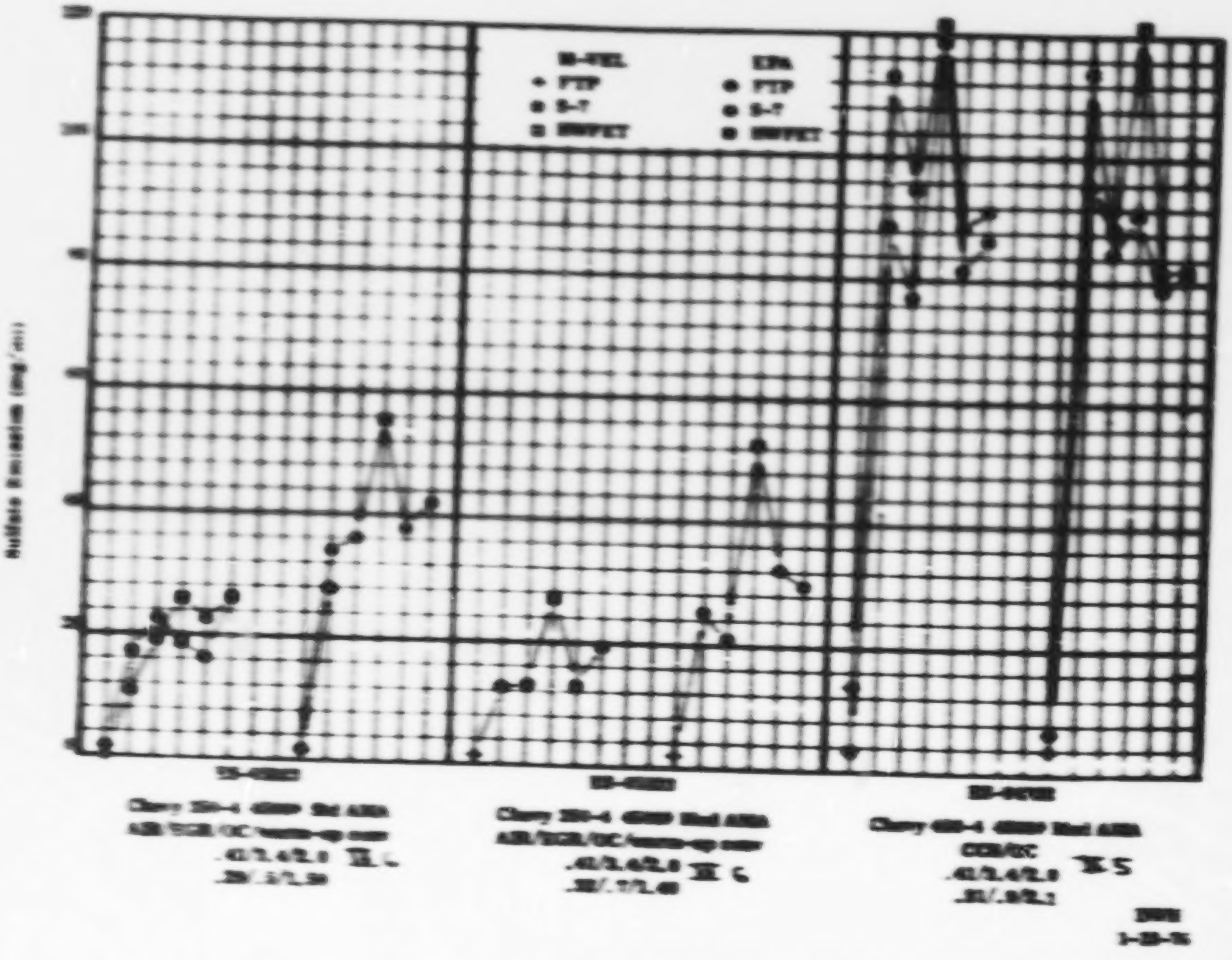
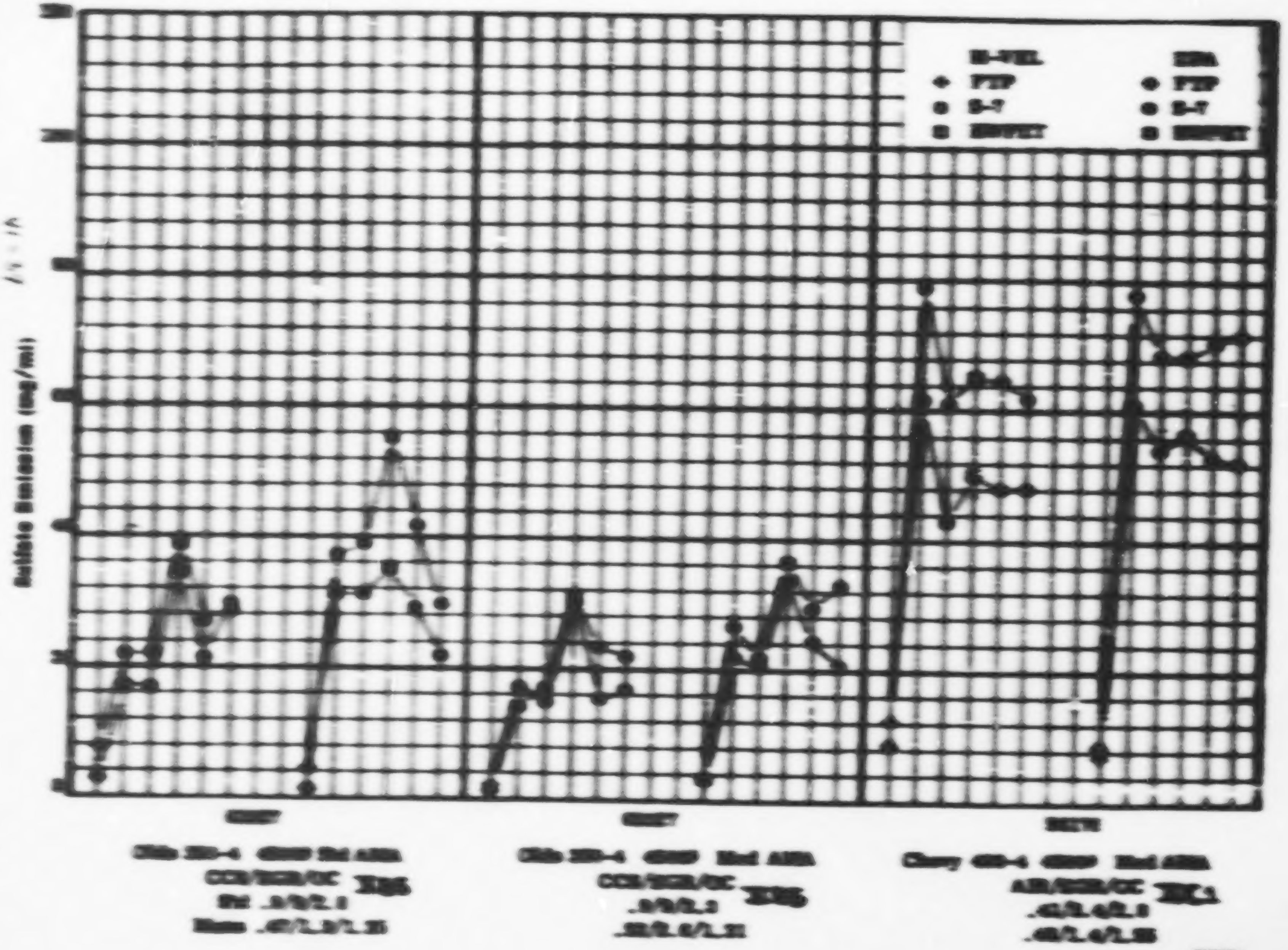


EPA Sulfate Baseline Program



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[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—	—	—	—
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible] Prototype Chrysler Imperial [illegible]
Electronic Lean Burn

TABLE 3

DATA SUMMARY

[illegible]

Run no.	Type	HC	CO	NOx	CO2	MPG	[illegible]	[illegible]	[illegible]	% Fuel S Conv. to [illegible]	[illegible]
[illegible]	[illegible]	.255	4.407	2.022	897.2	9.68	.2027	.112	.0002	95.3	.36
[illegible]	[illegible]	.175	2.466	3.121	537.1	16.7	.2075	.196	.0009	90.9	.50
[illegible]	[illegible]	.189	2.462	3.722	536.9	17.1	.2090	.197	.0026	102.0	.33
[illegible]	[illegible]	.250	2.552	2.508	651.1	18.9	.2028	.079	.0006	89.7	.30
[illegible]	[illegible]	.202	2.772	2.407	661.1	19.4	.2125	.192	.0023	92.3	.26
[illegible]	[illegible]	.215	2.771	3.126	574.9	16.6	.2013	.192	.0023	92.0	.17
[illegible]	[illegible]	.179	2.396	3.759	521.3	16.4	.2079	.207	.0022	96.1	.22
[illegible]	[illegible]	.209	5.192	2.799	790.6	10.6	-	-	-	-	-
[illegible]	[illegible]	.177	3.657	4.252	532.4	16.1	.2032	.171	.0008	109.0	.27
[illegible]	[illegible]	.190	5.398	4.586	525.6	16.2	.2075	.192	.0006	107.0	.21
[illegible]	[illegible]	.207	2.536	5.122	469.1	16.0	.2072	.190	.0003	111.4	.26
[illegible]	[illegible]	.200	2.675	5.221	590.2	16.7	.2030	.205	.0003	102.2	.23
[illegible]	[illegible]	.216	3.386	4.317	531.4	16.2	.2090	.173	.0004	110.0	.23
[illegible]	[illegible]	.207	3.389	4.679	530.5	16.1	.2026	-	.0004	-	.26

[illegible] Ford Maverick 400 [illegible]

DATA SUMMARY

		GM/MILE								% Fuel S Conv. to	
Run No.	Type	HC	CO	NOx	CO2	MPG	PART	SO2	SO4	SO2	SO4
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	505.3	16.8	.0348	.061	.0164	94.2	9.7
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	19.2	[illegible]	.061	.0588	69.8	45.4
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	21.8	[illegible]	.064	.0421	84.2	36.8
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	22.3	[illegible]	.073	.0448	73.6	46.4
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	21.5	[illegible]	[illegible]	.0465	100.2	42.0
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	19.6	[illegible]	[illegible]	.0388	57.6	28.3
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	19.3	[illegible]	[illegible]	[illegible]	59.0	33.4
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	14.5	[illegible]	[illegible]	.0265	35.1	55.5
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.8	[illegible]	.053	.0484	66.2	46.3
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	19.4		.030		43.0	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	21.4	[illegible]	.057	.0451	73.1	38.4
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	21.5	[illegible]	.053	.0347	68.8	39.6
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.7	[illegible]	.037	.0373	38.6	35.3
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	18.7	[illegible]	.038	.0364	47.9	28.5

[illegible] 266

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible] Ford Maverick [illegible] No. [illegible] (I.)

DATA SUMMARY

Run No.	Type	HC	CO	NOx	CO2	MPG	PART	SO2	SO4	SO2	SO4
				GRAMS/MILE						% Fuel S Conv. to	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	34.2	9.5
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	33.1	28.1
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	36.5	29.8
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	36.8	42.9
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	30.9	28.4
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	23.5	15.2
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	37.2	21.7
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	13.2	6.7
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	30.4	34.1
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	37.2	29.8
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	78.9	43.3
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	33.7	42.2
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	25.7	38.3
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	46.2	25.9

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DATA SUMMARY

Run No.	Type	HC	CO	NOx	CO2	MPG	PART	SO2	SO4	% Fuel S Conv. to SO2	SO4
[illegible]	LA-4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	HWFET	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	HWFET	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	LA-4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	HWFET	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	HWFET	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	S-7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

1976 Ford Maverick VID No. 6K91F172965

DATA SUMMARY

		GRAM/MILE								% Fuel S Conv. to	
Run No.	Type	HC	CO	NOx	CO2	MPG	[illegible]	SO2	SO4	SO2	SO4
5282	FTP	.556	2.979	1.577	587.7	14.7	.0020	[illegible]	.0069	22.7	4.7
5284	S-7	.288	.599	1.485	448.2	19.2	.0674	.026	.0077	30.7	29.2
5285	S-7	.296	.388	1.642	456.1	19.0	.0465	.019	.0073	27.8	16.3
5286	HFET	.265	.748	1.625	477.8	20.7	.0680	.024	.0087	34.0	25.6
5287	HFET	.242	.477	1.606	396.9	21.9	.0675	.030	.0098	38.5	27.9
5288	S-7	.272	.398	1.790	464.5	18.7	.0666	.017	.0057	18.1	23.7
5291	S-7	.798	.388	1.651	428.3	19.9	.0708	.017	.0077	20.5	25.5
5297	FTP	.488	2.159	1.809	574.2	15.2	.0478	.026	.0190	25.2	11.4
5290	S-7	.241	.407	1.685	459.0	18.9	.0673	.014	.0097	15.8	22.5
5292	S-7	.274	.460	1.602	456.5	18.9	.0477	.014	.0078	15.8	16.5
5293	HFET	.203	.465	1.570	384.6	22.5	.0760	.017	.0098	23.0	31.2
5294	HFET	.191	.582	1.667	385.7	22.5	.0747	.026	.0082	36.1	30.8
5295	S-7	.222	.398	1.758	465.2	18.6	.0387	.019	.0067	27.2	27.2
5296	S-7	.262	1.256	2.172	578.3	15.0	.0727	.019	.0070	17.1	16.3

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COMMENTS

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NOTE:

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Cooling – [illegible]

Preconditioning – [illegible]

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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]
[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	–	[illegible]	–	–	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

NOTE:

[illegible]

Cooling – [illegible]

Preconditioning – [illegible]

The test fuel was also [illegible] sulfur.

E CATALYST [illegible]

GM Sulfuric Acid Emission Data Group

[illegible]

CATALYST [illegible]

[illegible] SULFURIC ACID EMISSION DATA

[illegible]

[illegible]

[illegible]

[illegible] SULFURIC ACID [illegible]

[illegible]

[illegible]

[illegible]

Cooling – [illegible] fans in front of the vehicle and another fan at the [illegible] blowing across the vehicle from the passenger side.

Preconditioning – [illegible] miles of [illegible] driving schedule with [illegible] fuel [illegible] and the [illegible] miles of [illegible] with a [illegible] sulfur fuel.

Test fuel was [illegible] sulfur.

Manufacturer's Results:

[illegible]

VI-61

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] TAIL PIPE ON VEHICLE

[illegible] 1 STALL IN FIRST ACCEL. COLD START - [illegible]

[illegible] 1 STALL AT IDLE START [illegible]

[illegible] START [illegible]

NOTE: [illegible]

[illegible]

[illegible]

[illegible]
[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

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best available copy.

[illegible]

[illegible]

[illegible] SULFURIC ACID EMISSION DATA [illegible]
ENCLOSED [illegible]

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[illegible]

[illegible]

[illegible] [illegible] [illegible]

[illegible]

[illegible] [illegible] 1 FALSE START [illegible]

[illegible]

[illegible] 1 FALSE START [illegible]

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1.3 1.5 1.0

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